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MATERIALS SCIENCE AND ENGINEERING LABORATORY

FY 2005 PROGRAMS AND ACCOMPLISHMENTS

PolymERS Division

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NISTIR 7299

March 2006

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Executive Summary

I am pleased to report to you the results of a strong year for the Polymers Division. Our staff and researcher collaborators continue to be acknowledged for their work in important areas, and in my summary, I would like to note some of these recognitions received this year.

As an agency of the Department of Commerce, the National Institute of Standards and Technology (NIST) focuses on work, often in collaboration with industry, to foster innovation, trade, security, and jobs. This year, our efforts have been recognized by two awards specifically related to service to industry. Based on research, patenting, and technology transfer activities that resulted in commercialization of polymeric amorphous calcium phosphate compositions as dental restoratives, the Federal Laboratory Consortium (FLC) awarded **Joseph Antonucci** the 2005 FLC Award for Excellence in Technology Transfer. This prestigious award, judged by representatives from industry, state and local government, academia, and federal laboratories, recognizes outstanding work in transferring federal laboratory developed technology to industry. Also this year, the Secretary of Commerce awarded the Department of Commerce Silver Medal for Customer Service to the **NIST Combinatorial Methods Center**, specifically **Eric J. Amis**, **Kathryn L. Beers**, **Michael J. Fasolka**, **Alamgir Karim**, and **Christopher M. Stafford**, for excellence in transferring NIST-developed combinatorial and high-throughput measurement technologies to industry. Silver Medals are awarded to those individuals or groups that demonstrate exceptional performance characterized by noteworthy or superlative contributions that have a direct and lasting impact within the Department of Commerce.

Complementing these awards for service to industry, several scientists and engineers were acknowledged for their outstanding scientific careers. In a White House ceremony on June 13, 2005, **Michael J. Fasolka** was awarded the Presidential Early Career Award for Scientists and Engineers (PECASE), the nation's highest honor for professionals at the outset of their independent research careers. Mike was recognized for his experimental and theoretical studies of nanostructured polymer films and for investigations extending the power of next-generation scanned probe microscopy techniques on structures designed to provide quantitative measures of chemical, mechanical, and optoelectronic nanoscale material properties. At the 2005 Annual March meeting of the American Physical Society (APS), **Alamgir Karim** was named a Fellow of Society for his pioneering research on polymer thin films and interfaces, polymer brushes, blend film phase

separation, thin film dewetting, pattern formation in block copolymer films, and the application of combinatorial measurement methods to complex polymer physics. Acknowledging the breadth and impact of his extremely productive career, NIST named **Wen-li Wu** a Fellow of the Institute. Wen-li was specifically recognized for the impact of his advances in measurement methods to assist industry, developments in the fundamentals of scattering, and significant scientific insights in polymer physics.



Sampling of journal and book covers featuring research from the Polymers Division

This annual report provides a sample of the outstanding research from the scientists and engineers of the Polymers Division. I hope you enjoy reading our highlights in areas ranging from nanomanufacturing and nanofabrication to organic electronics and combinatorial methods. As usual, only a portion of our work is included in this report, so please visit www.nist.gov/polymers for more details. On our site, you can also download copies of any of our publications.

As always, I welcome your comments.

Eric J. Amis
Chief, Polymers Division

Direct Correlation of Organic Semiconductor Film Structure to Field-Effect Mobility

Organic electronics has dramatically emerged in recent years as an increasingly important technology encompassing a wide array of devices and applications including embedded passive devices, flexible displays, and sensors. Device performance, stability, and function critically depend upon charge transport and material interaction at the interfaces of disparate materials. Near-edge x-ray absorption fine structure (NEXAFS) spectroscopy is demonstrated as a powerful tool to quantify molecular orientation, degree of conversion, and surface coverage of solution-processed organic electronics materials as a function of processing variables and materials characteristics.

Dean M. DeLongchamp and Eric K. Lin

Organic electronic devices are projected to revolutionize new types of integrated circuits through new applications that take advantage of low-cost, high-volume manufacturing, nontraditional substrates, and designed functionality. Progress in organic electronics is slowed by concurrent development of multiple material platforms and processes and a lack of measurement standardization between laboratories. A critical need exists for diagnostic probes, tools, and methods to address these technological challenges.

Recent efforts towards large-scale adoption of organic electronics have focused on maximizing device performance using new molecular designs and processing strategies. In particular, tremendous effort has been directed towards solution-based processing strategies where fabrication under ambient conditions is possible. Significant progress has been made towards formulations for ink-jet printing, spin-coating, or dip-coating. However, rational design and systematic progress are hindered by insufficient correlations between organic semiconductor film structure and field-effect mobility in transistors.

Establishing direct correlations between the material structure and device performance has been challenging. These challenges are exemplified in recently developed soluble precursor molecules shown in Figure 1 that thermally convert into high-performance organic semiconductors. Conversion of precursor films involves changes in structure at many levels. First, the chemical structure changes as solubilizing groups are removed. Simultaneously, the molecules reorient with respect to the substrate. Finally, large-scale molecular reorganization causes the film to become thinner, eventually reaching monolayer and sub-monolayer

coverage. Each of these changes strongly impacts the performance of the semiconductor as an active layer in organic field effect transistors (OFETs).

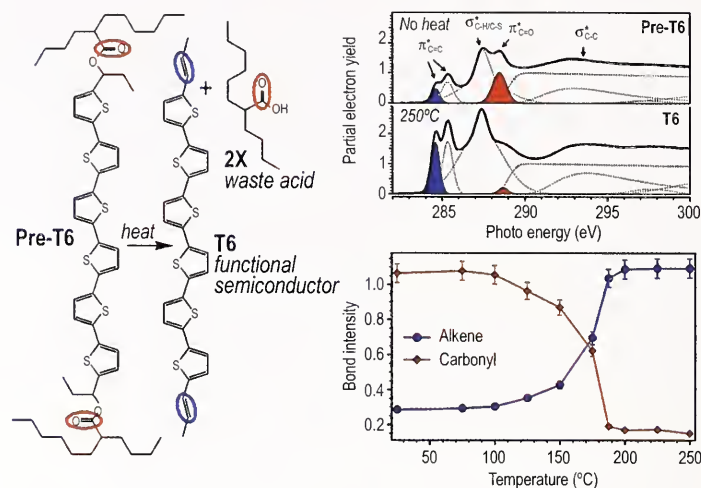


Figure 1: (Left) The conversion chemistry of an organic semiconductor oligomer from an organic solvent soluble species to an insoluble organic semiconductor. (Right) NEXAFS spectra illustrating quantification of the degree of conversion as a function of temperature.

To address these challenges, we developed and applied near-edge x-ray absorption fine structure (NEXAFS) spectroscopy to quantify the degree of conversion, molecular orientation, and surface coverage of organic semiconductor thin films. NEXAFS spectroscopy was performed at the NIST/Dow soft x-ray materials characterization facility at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory (contact: Daniel Fischer, NIST Ceramics Division). Carbon K-edge spectra were collected in partial electron yield (PEY) mode with a sampling depth of ≈ 6 nm. As cast, films of Pre-T6 in Figure 1 are approximately 20 nm thick. We expect the conversion, orientation, and defects within the sampling volume to closely match those of the mobile channel adjacent to the dielectric layer of field effect transistor devices.

Figure 1 shows the conversion chemistry of an oligothiophene that is initially soluble in organic solvents but undergoes thermolysis at elevated temperatures to become an organic semiconductor that is insoluble in organic solvents. The carbon K-edge spectra in Figure 1 exhibit peaks that quantify the degree of conversion. From these spectra, degrees of conversion between the precursor and product can be obtained over the full practical range of annealing temperatures. The NEXAFS spectra provide clear signatures of the conversion chemistry even in very thin films.

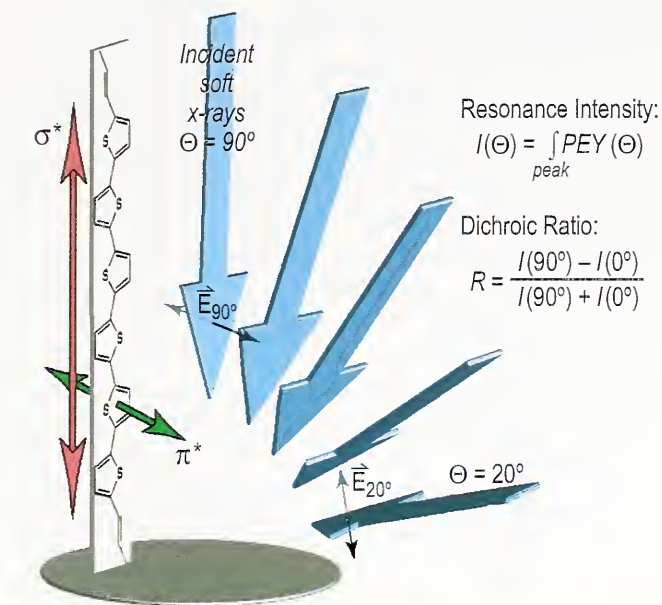


Figure 2: The geometry of near-edge x-ray absorption fine structure (NEXAFS) spectroscopy for the determination of the orientation of an oligothiophene organic semiconductor.

NEXAFS spectroscopy can also be used to measure the molecular orientation of oligothiophene molecules because the incident synchrotron soft x-rays are polarized. The carbon–carbon π^* and σ^* resonant intensities (Figure 2) exhibit a strong angular incidence dependence that corresponds to an oriented resonance defined by the spatial orientation of the final state orbital. The π^* intensity is largest at normal incidence (90°), indicating that the conjugated plane of the product tilts away from the substrate in an “edge-on” orientation. The σ^* intensity is greatest at glancing incidence (20°), indicating that the long axis is normal to the substrate in a “standing up” orientation.

The changes in molecular orientation accompanying thermolysis are quantified using a dichroic ratio, R , defined in Figure 2. R varies between +0.75 and –1.00, where a more positive R for the conjugated plane indicates increased tilt away from the substrate, while a more negative R for the long axis indicates greater surface-normality.

We observe four distinct orientation regimes during annealing, as shown in Figure 3. First, the precursor is vertically oriented, and this weak orientation persists until the treatment temperature of 125°C exceeds the melting point at 110°C . Second, R decreases from 125°C to 150°C . Third, R increases greatly between 150°C and 200°C , where the greatest increases in ester thermolysis are also observed, to plateau at 200°C . At this point, both the conjugated plane and the long axis of the molecule are angled away from the surface as depicted in Figure 2. Finally, R decreases again at 300°C indicating that the molecules relax into a more disordered orientation. This relaxation corresponds to coverage loss, which was also quantified with NEXAFS spectroscopy.

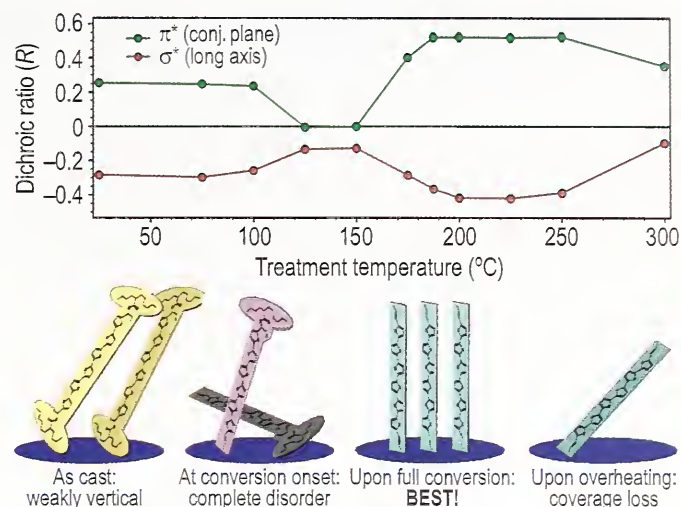


Figure 3: NEXAFS measurements of the orientation of the molecules as a function of temperature. The molecular orientation changes as the material undergoes chemical conversion.

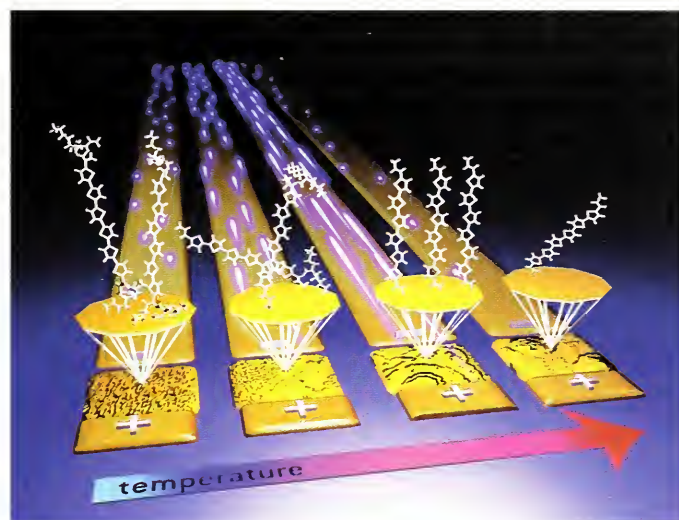


Figure 4: Graphical representation of the relationship between the degree of conversion and molecular orientation with the field effect mobility in a transistor device.

This example highlights NEXAFS as a powerful, nondestructive technique for detailed quantification of the structure and chemistry of nanometer thick organic semiconductor films. These data provided insight into, and direct correlations with, the changes in electronic properties. NEXAFS will continue to provide a powerful measurement platform for the systematic investigation of organic semiconductors and conductors.

For More Information on This Topic

D.M. DeLongchamp, S. Sambasivan, D.A. Fischer, E.K. Lin, P. Chang, A.R. Murphy, J.M.J. Frechet, and V. Subramanian, “Direct Correlation of Organic Semiconductor Film Structure to Field-Effect Mobility,” *Advanced Materials* **17**, 2340–2344 (2005).

Chaotic Flow to Enable Soft Nanomanufacturing

The challenge of generating nanoscale functional structures from soft materials (polymers, colloidal suspensions, dispersions) requires innovative manufacturing strategies. In our program, we utilize microfluidics to combine self-assembly technologies with top-down manufacturing methods. Proper mixing of components emerges as a crucial issue in microfluidic manufacturing operations due to the breakdown of conventional techniques. Our objective is to utilize the concept of “chaotic flow” for proper mixing of components.

Frederick R. Phelan, Jr. and Steve Hudson

A central goal of nanomanufacturing is to combine top-down manufacturing techniques with bottom-up methodology in a flexible and robust fashion. We are developing a portfolio of microfluidic-based techniques to accomplish this objective, focusing on particle self-assembly and *in-situ* monitoring of manufacturing operations.

An outstanding issue in a wide variety of manufacturing operations is the efficient mixing of liquid phase chemical species. Due to the small length scales of the flow channels (from 1 μm to 200 μm), the typical turbulent mixing, which is extensively utilized in larger scale flows, cannot be achieved, and new schemes must be developed. It is known that *chaotic flow* is the most efficient way of mixing outside the turbulent regime. In microfluidics, little is known about how to generate chaotic flow and how to best measure it. Here we describe numerical methodologies that demonstrate chaotic flow in microfluidic geometries. We find the *signatures of chaos* via detailed analysis of the flow fields and show that we can generate chaotic flow for both pressure-driven and electric field-driven flows.

To generate chaos in microfluidic flows, we exploit the *principle of temporally crossing streamlines* which states that a necessary condition for generating chaotic flow is that the streamlines at time t must intersect the streamlines at some later time $t + \Delta t$ at one or more points in the flow domain. The crossing streamlines considered in this work are distinctly different from those considered in previous studies. We considered here the case of *flow in intersecting channels*, where temporal variations are introduced through the use of oscillatory flow boundary conditions.

Both batch and continuous mixing have been studied, as they both have direct relevance to processes of interest. For batch mixing, the simplest case of

intersecting channels is a cross flow mixer (CFM) as shown in Figure 1. To generate chaos in this geometry, flow in the two perpendicular channels of the cell is driven sinusoidally, and 90° out of phase. Thus, successive sets of temporal streamlines cross each other every quarter period at the center of the geometry, as required for chaos per the crossing streamline principle.

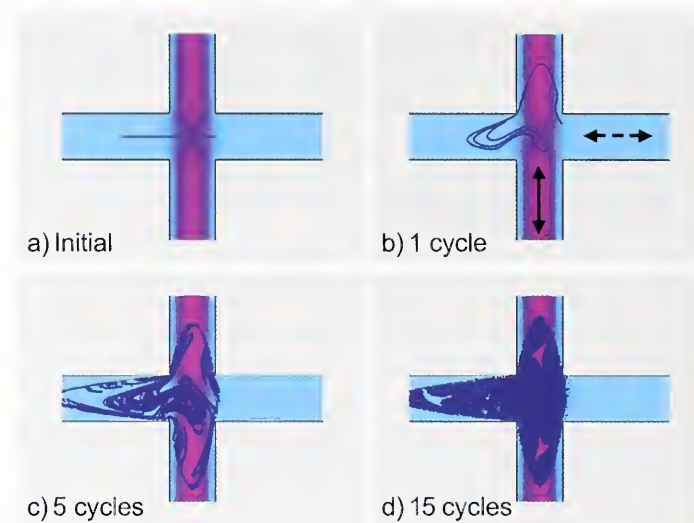


Figure 1: Chaotic mixing in a pressure-driven cross flow mixer (CFM), for a Strouhal number of 1.28 after 15 cycles. A material line composed of 25,000 particles is initially stretched out along the x-axis. The stretching and folding of the material line leads to kinematic particle dispersion, a signature of chaotic flow.

Conventional methods fail in the analysis of chaotic flow. Thus, in order to evaluate the ability of a flow configuration to produce chaotic motion, the deformation of material lines or surfaces composed of passive tracer particles are tracked in a manner analogous to flow experiments using tracer dyes. The deformation of a material line composed of 25,000 individual particles in the CFM is shown in Figure 1. The material line is initially stretched out along the x-axis (Figure 1a), and the stretching and folding of the material line gradually leads to the particle dispersion pattern shown in Figure 1d.

From the deformation of the material line, we may identify three signatures of chaos. First, from the figure we see that the particles tend to evolve to a formation in which they are randomly dispersed in a closed surface within the flow domain — this is a signature of *Hamiltonian chaos*. A second signature is the exponential stretching of the line of particles. A semi-log plot of L/L_0 vs. time (where L is the length of the line) shows that the data are very closely fit by an exponential relationship with a positive exponent value of 0.41, which can be thought of as an “effective” or

finite-time *Lyapunov exponent*. A final signature of chaos is that the flow is *ergodic* — that is, the dispersion patterns observed after a large number of cycles for different particle initial conditions are indistinguishable from one another. Simulations with different particle initial conditions confirm the ergodic property.

The onset of chaotic behavior in the CFM is controlled by a dimensionless number called the Strouhal number (St) which relates the distance a particle moves in a half-cycle to the width of the flow channel. Chaos sets in at $St \approx 0(1)$, and the size of the chaotic region and magnitude of the Lyapunov exponent grows continually with increasing St . Further, we identified that the mechanism for chaotic flow in the CFM is a periodic combination of stretching and rotation, making the system a *continuous tendril-whorl (TW)* type flow. This differentiates it from other studies using oscillatory boundary conditions as they produce discrete (non-continuous) TW flows resulting in the requirement of greater geometric complexity to mix the fluid streams.

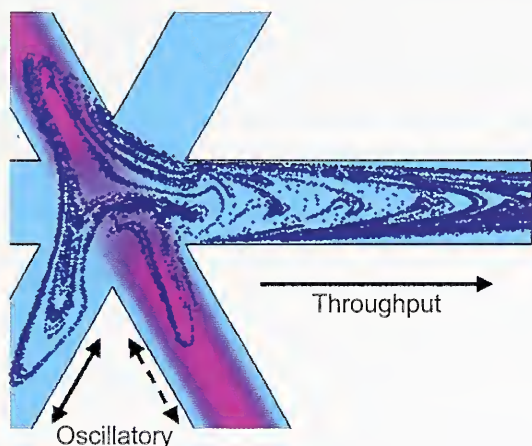


Figure 2: Chaotic mixing in the star-cell geometry is shown for a Strouhal number of 1.28 and a velocity ratio of 0.125 after 10 cycles. In the star-cell, chaos is generated by the oscillatory flow in transverse channels, and the lateral flow provides throughput for continuous mixing.

We now discuss continuous chaotic mixing, which will be relevant to any continuous high-speed nanomanufacturing operation. In a configuration called the star-cell geometry (see Figure 2), a lateral continuous channel flow (from left to right) is combined with the oscillatory cross flow. The mixing characteristics in the star-cell are a function of both St and the ratio of the continuous-to-oscillatory velocity. The deformation of a material line passing through the oscillatory section is shown in Figure 2. The particle dispersion in the downstream channel indicates that the competition between the two flows is quite effective in producing a well-mixed effluent.

Clearly, the configuration may also be used with a discontinuous throughput stream, to mix components on a semi-batch basis.

The results discussed above are for pressure-driven flow. However, an important means of transporting fluid in microfluidic geometries is through the use of electroosmotic flow (EOF), especially in the emerging area of droplet-based microfluidics. In the EOF flows, temporally crossing streamlines are generated by application of out-of-phase sinusoidal voltage gradients.

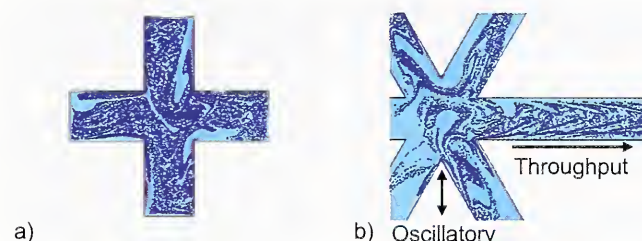


Figure 3: a) Chaotic mixing in an EOF driven cross-flow mixer (CFM), for a Strouhal number of 0.64 after 10 cycles. b) Chaotic mixing in an EOF driven star-cell mixer, for a Strouhal number of 2.04 and a velocity ratio of 0.125 after 10 cycles. For both cases, the oscillatory flow is driven by the application of out-of-phase sinusoidal voltage gradients along the major axes of the cell.

We find that chaotic mixing can also be obtained in EOF, for both batch and continuous flow. Stretching of a material line for batch mixing via EOF is shown in Figure 3a and for continuous mixing in the star-cell in Figure 3b. Chaotic particle dispersion and positive Lyapunov exponents are observed for both cases. In terms of experimental implementation, the EOF driven flow offers several advantages. First, the ends of the oscillatory channels are closed, so there are no inflow and outflow to handle. Second, the oscillatory flow channels can be made shorter for EOF, as it was found that the critical Strouhal number for the onset of chaos decreased and the effective Lyapunov exponent increased, as the ratio of the length to the width of these channels was made smaller.

Experimental testing of these results is currently being conducted as well as an investigation of the interplay between diffusion and chaotic flow.

For More Information on This Topic

F.R. Phelan, Jr., N.R. Hughes, and J.A. Pathak, "Analysis of the Mechanism for Chaotic Mixing in Oscillatory Flow Microfluidic Devices," submitted to *Phys. Rev. Lett.*, 2005.

F.R. Phelan, Jr., N.R. Hughes, and J.A. Pathak, "Mixing in Microfluidic Devices Using Oscillatory Channel Flow," submitted to *Physics of Fluids*, 2005.

X-ray Reflectivity as a Tool for Characterizing Pattern Shape and Residual Layer Thickness for Nanoimprint Lithography

Nanoimprint lithography has the potential for high throughput patterning with an ultimate resolution of better than 10 nm. With these length scales, our ability to pattern greatly exceeds our ability to quantitatively evaluate the quality of the patterning process. Measurements that can evaluate the fidelity of the pattern transfer process and the overall quality of the imprint are critical for realizing the full potential of nanoimprint patterning techniques.

Christopher L. Soles and Ronald L. Jones

Nanoimprint Lithography (NIL) is a form of printing whereby nanoscale features are written into a master, typically Si, quartz, or some other hard material, using a slow, high-resolution technology such as e-beam lithography. The master can then be rapidly and repeatedly stamped into a softer resist film. This replication technique is a cost-effective way to combine the high-resolution patterning of e-beam lithography with the throughput of a stamping or printing process.

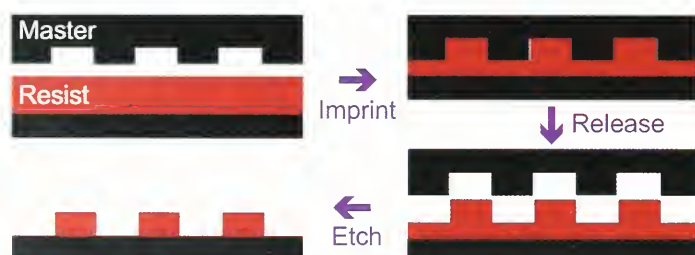


Figure 1: Schematic of nanoimprint lithography process.

The resolution of NIL is comparable to that of e-beam lithography, and features as small as 10 nm have been demonstrated. However, it is difficult to quantify and control dimensions in such small features. To take full advantage of the potential resolution of NIL, high-resolution shape metrologies are critical. Furthermore, during the imprint process, the master is unable to fully displace the resist and make contact with the substrate. This leaves a residual layer of resist between the features that can be removed with a reactive ion etch. However, this also laterally erodes the feature width. Minimization of this lateral trimming and control of the final feature size requires a precise knowledge and optimization of the residual layer thickness. In short, two of the most pressing issues facing NIL include: (1) quantifying the fidelity with which the patterns in a master are transferred to the imprinted film; (2) quantifying the residual layer thickness. Here we adapt specular x-ray reflectivity (SXR) to quantify both the fidelity of pattern transfer and the residual layer thickness with nanometer precision in NIL masters and patterns.

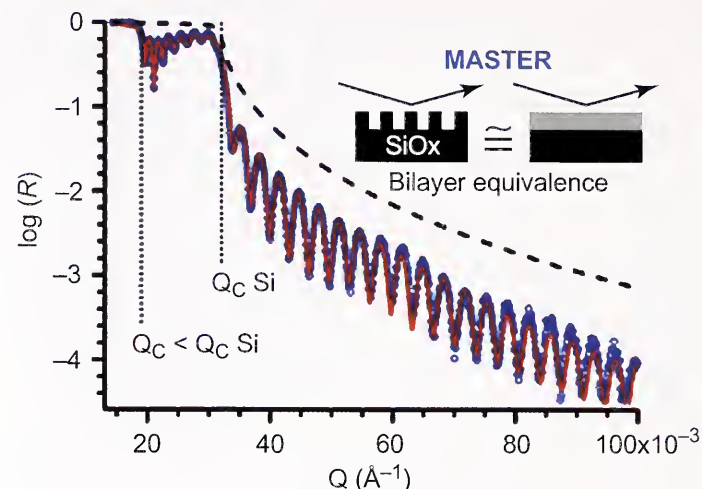


Figure 2: SXR data from a NIL master. $Q=2\pi/\lambda \sin(\theta)$ with λ the wavelength of the incident radiation and θ the grazing angle.

SXR is a well-established method for measuring both the thickness and the density as a function of depth into a thin film. Here we extend the use of SXR to patterned films where the lateral length scales of the patterns are in the sub μm range. As the cartoon in the inset of Figure 2 indicates, the master or mold is comprised of a single material, SiO_x (black). However, the reflectivity, R , is characteristic of a bilayer film, a smooth “gray” film on the black SiO_x . The strong, periodic Kiessig fringes and the two critical angles Q_C are consistent with a smooth bilayer structure. The red line through the blue experimental data points is a fit to such a smooth bilayer model where the density of the gray layer is an average of the white and black (open and fully dense) regions of the pattern while the thickness of the gray layer equals the pattern height. The SXR averages density over length scales that are apparently larger than the lateral-length scales of the topology.

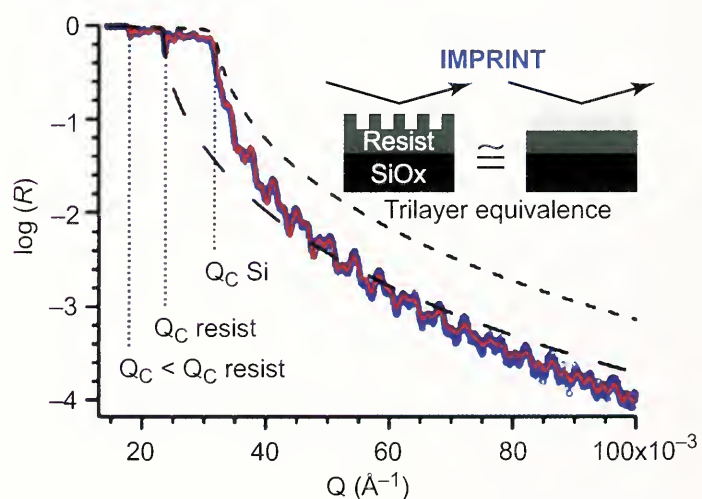


Figure 3: SXR data from a polymeric resist imprint created from the master characterized in Figure 2.

Analogous SXR measurements are repeated on a polymeric resist imprint created from the master above. These reflectivity data are shown in Figure 3. Consistent with the mold, the reflectivity from the imprint on the SiO_x substrate shows characteristics of a smooth trilayer structure. The Kiessig fringes show a beating of multiple periodicities, and three Q_c 's are observed. The cartoon in the inset indicates black for the SiO_x substrate, dark gray for the pure resist, and light gray for the patterned region of the resist. As before, the light gray is an average of the dark gray (solid) and white (open) domains. The red solid line through the blue experimental data is a quantitative fit to a smooth trilayer model.

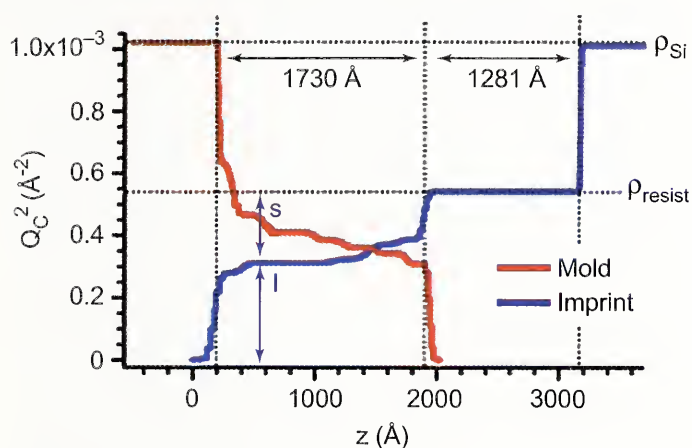


Figure 4: Scattering length density profiles as a function of distance vertically through the patterns for the mold (red) and the imprint (blue). The horizontal axis is arbitrarily assigned, so the mold substrate on the left ($\approx 0 \text{ Å}$) faces the imprint substrate on the right ($\approx 3100 \text{ Å}$) with the mating pattern region in between.

The scattering length density Q_c^2 profiles as a function of distance vertically through the patterns (z) are shown in Figure 4. Q_c^2 is directly proportional to mass density, and the horizontal dotted lines indicate the values of Q_c^2 for the pure SiO_x and the resist. On the density profile for the imprint, the region (1281 ± 10) Å wide matching the full density of the resist represents the residual layer thickness. To the left of this is a region of reduced density that is (1730 ± 10) Å wide. This is the height of the pattern. One can also see how the depth of the patterns in the mold equals the height of the imprinted pattern; this indicates complete mold fill. Such a comparison of the mold and imprint can be used to quantify the fidelity of pattern transfer.

There are two blue vertical arrows drawn next to the profile of the imprint. Line “l” starts at $Q_c^2 = 0$ and extends vertically to the intersection of the imprint profile. Line “s” starts at this same intersection and extends vertically to the Q_c^2 value corresponding to the density of the pure resist. At any z , the ratio $l:s$ defines the line-to-space ratio of the pattern. This ratio increases with z for the imprint, indicating that the pattern is narrow on the top and broadens near the residual layer. A similar construction can be made for the mold although the lines are not shown

here. Through these density variations as a function of pattern height, the pattern cross-sections can be evaluated.

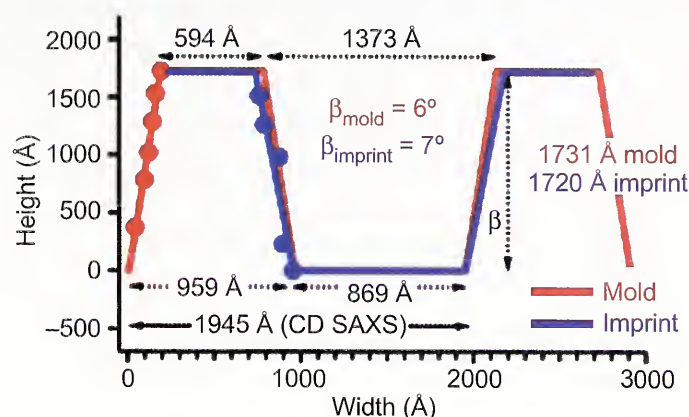


Figure 5: Comparison of mold and imprint profiles. The red and blue data points indicate the line shape profiles from the SXR for the mold and imprint, respectively. The corresponding physical models that best fit the data are indicated by the solid lines. For the sake of clarity, the mold data are shown on the left side of one of the features while the imprint data are shown on the right.

These line width variations as a function of pattern height are relative, and one cannot define an absolute line width from the SXR alone. An external calibration of the line width, space width, or pattern pitch is needed to convert the relative line-to-space variations into absolute values. To illustrate this, critical-dimension small angle x-ray scattering (CD-SAXS) was used to quantify the pattern cross-section. A trapezoidal line shape provided an excellent fit to the CD-SAXS data. Figure 5 is the resulting comparison that shows how well the imprint features fit into the mold, indicating an excellent fidelity of transfer. The pitch of 1945 Å from the CD-SAXS models is used to transform the relative line-to-space ratios from the SXR density profiles into physical line widths. These SXR data points exactly coincide with the solid lines for the CD-SAXS models, showing excellent agreement in terms of both pattern height and the trapezoid side wall angles β .

In summary, SXR is a powerful metrology to quantitatively characterize the residual layer thickness and the relative line-to-space ratio variations as a function of pattern height. If one of the widths (line or space) or pattern pitch is known by some other technique (CD-SAXS, SEM, AFM, etc.), these relative line-to-space ratios can be quantified in terms of an absolute length scale to completely define the pattern cross-section. Applying this metrology to both the mold and the imprint makes it possible to not only quantitatively measure the residual layer thickness but also assess the fidelity of pattern transfer.

For More Information on This Topic

H.J. Lee, C.L. Soles, H.W. Ro, R.L. Jones, E.K. Lin, W.L. Wu, and D.R. Hines, *Appl. Phys. Lett.* **87**, 263111 (2005).

Gradient Libraries of Surface-Grafted Polymers: Combi Tools for Surface Functionality

Advanced applications, such as friction and wear management in microelectromechanical systems (MEMS), adhesion promotion for coatings, protein adsorption control in biomaterials, and environmentally responsive surfaces for sensors require tunable, well-defined interfaces. Layers of grafted polymers provide means for physically robust, chemically versatile surface functionalization. While recent advances in controlled polymerization enable grafted polymers that exhibit many types of architecture and composition, identifying the optimal grafted system for a given application can be difficult, time consuming, and expensive.

Kathryn L. Beers and Chang Xu

Through the NIST Combinatorial Methods Center (NMC), the Polymers Division has developed new tools for probing the optimal molecular- to micro-scale properties of grafted polymer systems. These methods employ microfluidic technology to deliver tailored mixtures and sequences of monomers to an initiator-functionalized surface. The resulting grafted polymer *libraries* exhibit gradual, systematic changes in composition, chain length, and architecture. Gradients of grafted *block copolymers* prepared via these techniques reveal composition regimes that “switch” their surface properties in response to solvent exposure. Moreover, our unique method for preparing *statistical copolymer* composition gradients provides comprehensive maps of complex surface chemistry that were previously impossible.

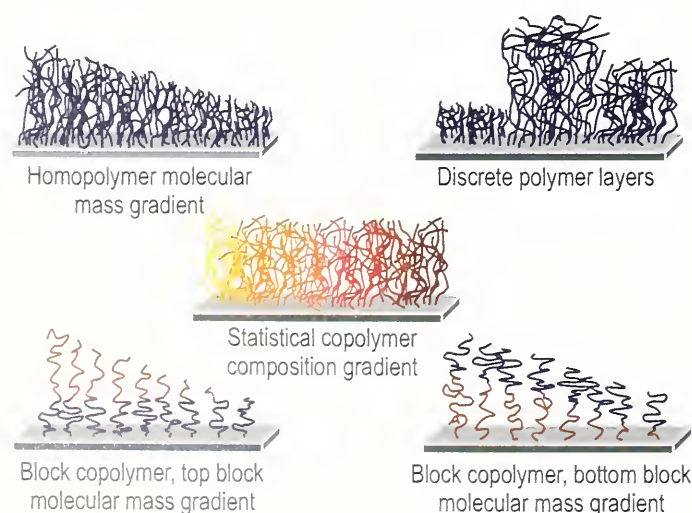


Figure 1: Examples of polymer libraries prepared using micro-channel confined surface initiated polymerization (μ SIP) and ATRP of methacrylates.

Using shallow channels ($< 500 \mu\text{m}$ in height) to confine fluids over initiator-functionalized surfaces suppresses mixing. By controlling the composition of fluids pumped into the channels, and the length of time of surface exposure, gradients in composition or relative molecular mass are produced. This technique, micro-channel confined surface initiated polymerization (μ SIP), was used to produce a variety of combinatorial surfaces as shown in Figure 1 and enables systematic measurement of polymerization parameters.

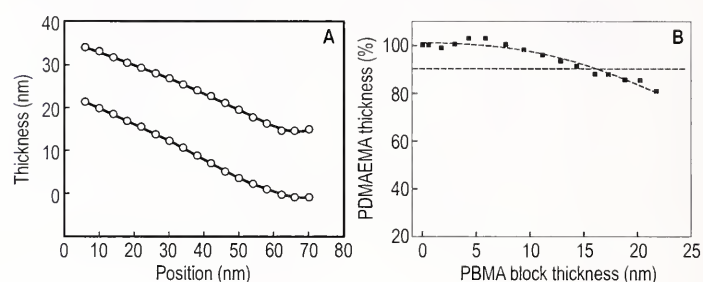


Figure 2: A) Film thickness of gradient poly(*n*-butyl methacrylate) (pBMA) homopolymer (closed symbols) and poly(*n*-butyl methacrylate-*b*-*N,N*-dimethylaminoethyl methacrylate) (p(BMA-*b*-DMAEMA)) (open symbols). B) Percentage growth of PDMAEMA block on the gradient surface with respect to a bare initiator-modified surface.

The initiation efficiency of a homopolymer on a surface affects both the density and relative molecular mass distribution of the second block that can be grown from it. Figure 2A shows data from a relative molecular mass gradient of poly(*n*-butyl methacrylate) (pBMA) that was uniformly chain extended with poly(*N,N*-dimethylaminoethyl methacrylate) (pDMAEMA) to form the block copolymer poly(*n*-butyl methacrylate-*b*-*N,N*-dimethylaminoethyl methacrylate) (p(BMA-*b*-DMAEMA)).

A relative measure of initiation efficiency was obtained as a function of molecular mass of the bottom pBMA block by normalizing the change in thickness of p(BMA-*b*-DMAEMA) to the thickness of pDMAEMA grafted directly from a separate initiator-functionalized surface. The data in Figure 2B show that the efficiency remains above 90 % for pBMA with a thickness of 15 nm or less, indicating that comparative measurements of block copolymer behavior are possible below this thickness. Using this information, a series of surface-grafted block copolymer gradients was prepared with pBMA as the bottom block and pDMAEMA as the top block.

Figure 3A shows data from three gradient surfaces with different, uniform bottom block thicknesses and similar gradients in top block thickness. The surface energy, as

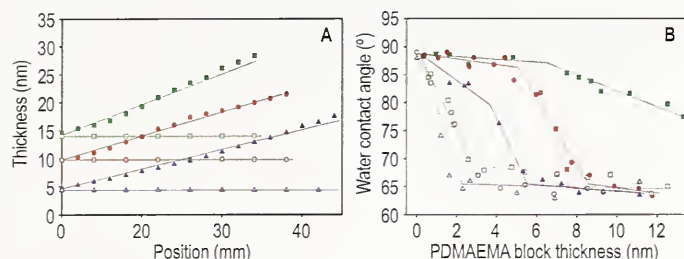


Figure 3: A) Thickness profiles of three gradient surfaces of *p*(BMA-*b*-DMAEMA) prepared via μ SIP. B) Solvent response behavior of *p*(BMA-*b*-DMAEMA) in water (open symbols) and hexanes (closed symbols) as a function of relative molecular mass of the top (pDMAEMA) block for three thicknesses of pBMA bottom block. Colors and symbols correlate solvent response profiles to samples mapped in Figure 3A. Lines drawn to aid reader's eyes.

measured by water contact angles, of the air interface of the brush layer can be controlled by exploiting solubility differences between pBMA and pDMAEMA. In water, the pDMAEMA chain segments swell, while the pBMA segments collapse. After drying, the surface exhibits the same water contact angle as pDMAEMA homopolymer brushes as long as there is at least (2 to 3) nm of pDMAEMA in the copolymer to cover the surface (Figure 3B, open symbols). After exposure to hexanes, which will swell the lower pBMA chain segments and collapse the pDMAEMA segments, the pBMA segments can be expressed at the surface, covering the pDMAEMA segments. The main requirement for this “surface response” is a ratio of pBMA to pDMAEMA sufficient for complete rearrangement and pBMA surface coverage, as shown in Figure 3B. At intermediate ratios, a partial expression of the lower pBMA produces a range of intermediary surface energetics.

Determination of the composition range for this transition, its dependence on chain length, and optimization of the response region were all possible using the gradient method. Performing measurements on single gradient specimens reduced variability and illuminated the subtlety and sensitivity of the transition to relative molecular mass and copolymer mass fraction.

Well-defined surface chemistry has been used to control structure formation in thin films and fluid flow in microfluidic devices. To map and optimize these effects, controlled, smooth gradients in chemical expression have been produced with self assembled monolayers (SAMs). However, SAM surfaces offer a limited number of functional groups and modest stability over time. Polymer brush layers provide means to expand the chemical diversity of surface gradients while creating a layer of carbon chains to protect the hydrolytically unstable silicon oxygen bonds that covalently link the chains to the surface. A compelling case is a gradient in statistical copolymer composition, for which we have recently developed a fabrication strategy using μ SIP.

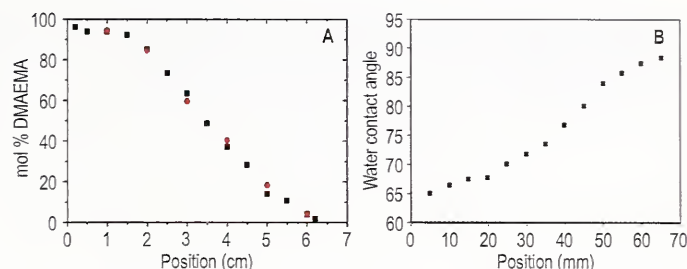


Figure 4: A) Stability of a monomer composition gradient inside a microchannel monitored by Raman spectroscopy at 0 h (black squares) and 2 h (red circles). B) Water contact angle of *p*(BMA-co-DMAEMA) as a function of position on a gradient of composition prepared from the solution gradient mapped in Figure 4A.

A gradient in solution composition was constructed such that the monomer feed was varied from (2 to 98) % by volume DMAEMA relative to BMA along the channel (Figure 4A). Both the establishment and stability of the solution gradient were measured by Raman spectroscopy, indicating that the gradient persisted for at least 2 h, while the reaction time was only 40 min. Figure 4B shows water contact angle measurements taken along the polymerized gradient, which reveal a smooth transition from the surface energetics characteristic of pDMAEMA to those of pBMA. The changing composition of the polymer brush was also characterized by NEXAFS measurements (data not shown). Unlike the block copolymers, the statistical copolymer surface does not switch the surface expression with exposure to different solvents. The chemical gradient is trapped by the intimately mixed nature of the copolymerization.

Fabrication of *grafted tapered copolymers*, which exhibit a gradual change in composition along the polymer chain, has also been demonstrated. An upcoming publication will describe the fabrication and properties of this unique system. In addition, future work includes combining micro-scale patterning with the chemical gradient brushes for the fabrication of calibration specimens, as well as expanding the method to additional monomer types and polymerization mechanisms to make μ SIP a versatile, widely applicable measurement tool.

For More Information on This Topic

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Or visit the NCMC website (www.nist.gov/combi)

Quantifying Cellular Response to Biomaterials with Macromolecular Assembly

In order to move beyond empirical trial and error into design, biomaterials development is in urgent need of reliable measurement standards and techniques. These depend on the ability to quantify protein-mediated cellular response to technologically relevant materials. We introduce a multi-molecular assembly of polymer/protein gradients as a technique to do just that. We demonstrate its potential to study interactions between fibroblasts, a particular polymeric biomaterial, and fibronectin. However, we emphasize the ease of extending the technique to quantify interactions between a variety of biomedically relevant polymers, proteins, and cells.

Ying Mei, Lori Henderson, and Jack R. Smith

The competing issues of reproducibility and applicability in measurements of cellular response must be addressed by the biomaterials industry. Information generated by experimental testing needs to be quantitatively robust, however, the inherent variation in the response of any biological organism and the complexity of protein/surface interactions are problematic; most currently used biomaterials lack a homogeneous or well-determined surface; efforts to quantify biological response have focused on using regular and simplified model surfaces, such as those of self-assembled monolayers (SAMs); and the fact that polymers of direct interest in biomedical applications cannot be incorporated into SAMs renders the practical applicability of these results questionable.

To address these issues, we synthesized a surface incorporating a biomedically relevant polymer, poly(2-hydroxyethyl methacrylate) [poly(HEMA)], through a multi-macromolecular assembly (MMA). We use automated fluorescent microscopy to demonstrate that the system is sufficiently well-defined for quantifiably repeatable measurements of cell response and protein adsorption. We have described the latter phenomenon to a high degree of accuracy with a simple, geometric model.

Preparation of the MMA gradient sample is conceptually simple. First, a SAM of octyltrichlorosilane (OTS) is deposited on a silicon substrate by evaporation. Then, the wafer is placed upright in a reaction vessel where atom transfer radical polymerization (ATRP) initiator is pumped in at a specific rate (Figure 1a). Filling from the bottom creates a differential exposure to the initiator along the length of the sample parallel with the walls of the vessel. This leaves a grafting density (σ) gradient of poly(HEMA) on the surface of

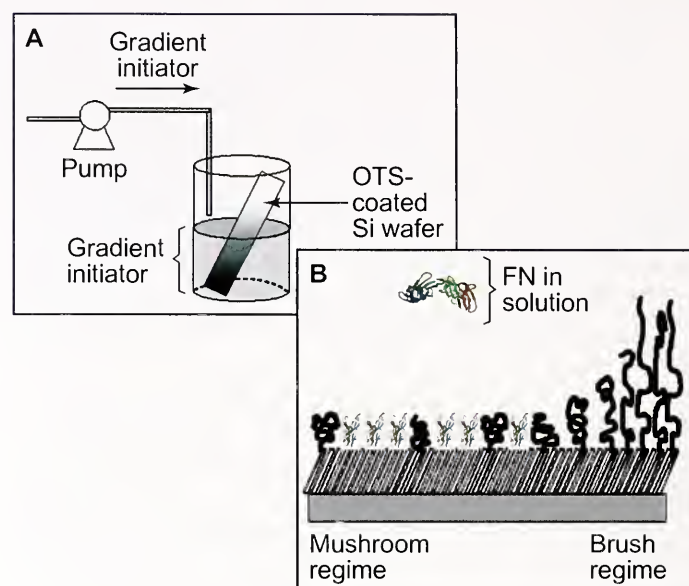


Figure 1: A) Schematic illustration of the reaction vessel used in the preparation of the gradient of polymerization initiator. B) Schematic illustration of poly(HEMA) conformational change from "mushroom" regime to "brush" regime on the gradient surface. Poly(HEMA) is represented in black, while FN is schematically represented by the multi-colored structures. OTS is represented as an unfilled rectangle. ATRP initiator is represented as a gradually filled rectangle.

the sample in the direction parallel to the walls of the reaction vessel (Figure 1b). Subsequently, the sample is removed from the vessel and exposed to fibronectin (FN) solution. Later, the samples are seeded with fibroblast NIH-3T3 cells in medium.

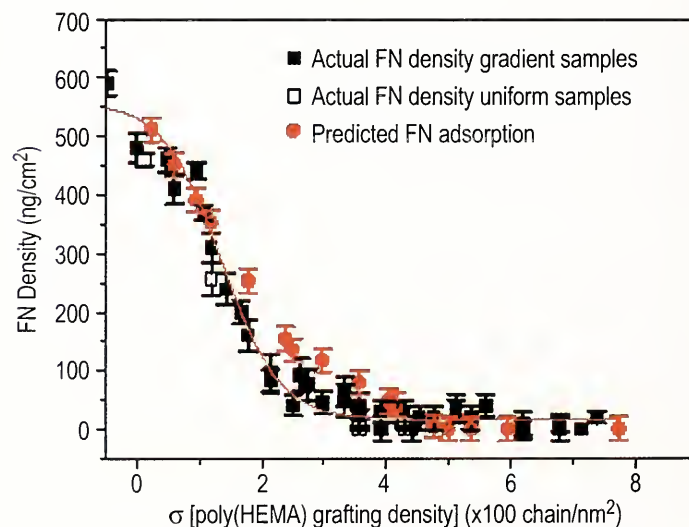


Figure 2: FN density vs. σ . Black data points are averaged results from three gradient or twelve uniform (non-gradient) samples. FN density was estimated from measurements of the thickness of the adsorbed layer obtained via ellipsometry. Data in red were obtained from the geometric model of poly(HEMA) surface coverage.

FN adsorption (FN_{ads}), measured using variable angle spectroscopic ellipsometry, was found to vary sigmoidally with σ (Figure 2). A simple geometric model, in which FN_{ads} is proportional to the area of the surface left uncovered by polymer, predicted the former with a r^2 coefficient of 0.97 (Figure 2). In the model, the surface coverage of poly(HEMA) is estimated from σ obtained from ellipsometry measurements performed prior to FN exposure and the radius of gyration of poly(HEMA).^[1]

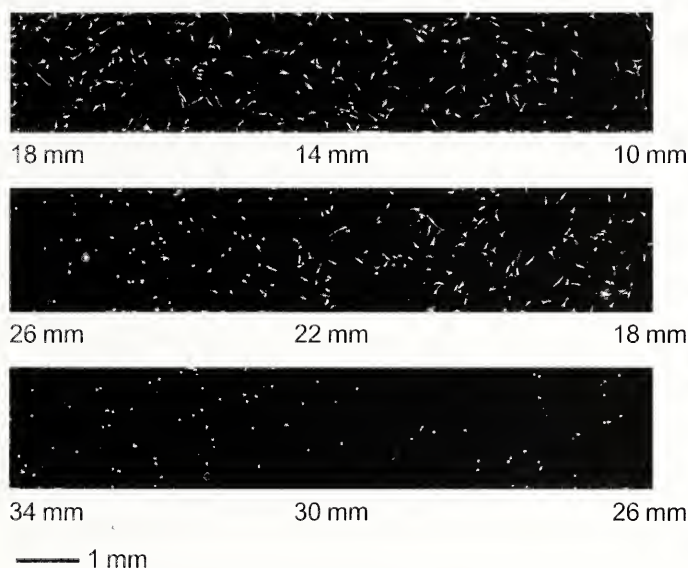


Figure 3: Fluorescence microscopy image of stained fibroblast NIH-3T3 cells seeded on a FN pre-coated σ gradient sample. Although the sample is contiguous, its microscopy image here is split into three segments so that changes in cell morphology with distance/ σ will be visible on the page. Distance in the Figure is measured from the end of the sample closest to the top of the reaction vessel (i.e., from the end of the sample with lowest σ in Figure 1a).

Cellular response varied dramatically along the surface of the poly(HEMA)/FN gradient (Figure 3). As cell spreading (Figure 4) and FN_{ads} (Figure 2) were both found to vary sigmoidally with σ , the high degree of correlation between the two phenomena was clearly demonstrated. The onset of maximal cell adhesion and cell spreading were measured at FN_{ads} of 50 ng/cm^2 and 100 ng/cm^2 , respectively. Further, a ten-fold increase in σ caused a change in the average area of fibroblasts (i.e., cell spreading) from 1238 ± 704 to 377 ± 216 μm^2 . The standard deviation represents the variation of the measurement over 12 trials.

Results obtained on three separate gradient samples were in quantitative agreement with those obtained on uniform (i.e., non-gradient) samples of similar composition (Figure 2 and 4). This shows the capability of the former to dramatically advance the pace of biomedical materials research through simultaneous testing of multiple compositions.

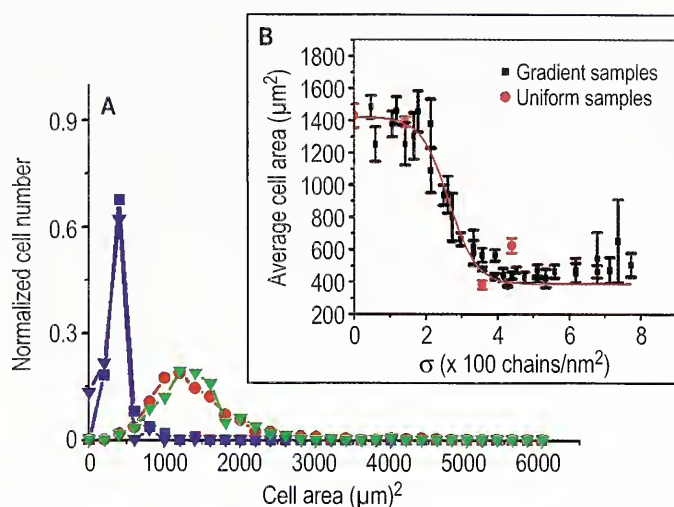


Figure 4: a) Histogram of cell size on various FN coated surfaces: bare OTS (green), low (red), high (blue, purple). b) Inset: Change in cell spreading (area) with σ

Although combinatorial studies have already received significant attention in biomaterials research, their use is limited by the lack of a complete toolbox including streamlined sample preparation, characterization, bioactivity assay, and data analysis. We demonstrate the uses of gradient preparation technology, controlled cell culture, automated fluorescence microscopy and quantitative image analysis to generate a database for combinatorial investigation of the effect of σ on cell adhesive protein adsorption, fibroblast adhesion, and spreading.

In addition, adsorption profiles of different biological macromolecules and their interactions with surface chemistries can be quantified by simply replacing FN in the pre-adsorption part of this experiment. In fact, we are currently using the approach presented here to investigate poly(HEMA)/fibrinogen gradients and will do so with other extracellular matrix proteins. MMA has few limitations regarding the variety of cells in the experiment; therefore the combination of MMA technology, quantitative fluorescence microscope, and controlled cell culture provides the foundations for the cell informatics about material properties, protein adsorptions, and cellular responses.

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Nanometrology

Nanotechnology will revolutionize and possibly revitalize many industries, leading to new and improved products based on materials having at least one dimension less than 100 nm. The federal government's role in realizing the full potential of nanotechnology is coordinated through the National Nanotechnology Initiative (NNI), a multi-agency, multi-disciplinary program that supports research and development, invests in a balanced infrastructure, and promotes education, knowledge diffusion, and commercialization in all aspects of nanoscale science, engineering, and technology. NIST's unique and critical contribution to the NNI is *nanometrology*, defined as the science of measurement and/or a system of measures for nanoscale structures and systems. NIST nanometrology efforts focus on developing the *measurement infrastructure* — measurements, data, and standards — essential to advancing nanotechnology commercialization. This work provides the requisite metrology tools and techniques and transfers enabling measurement capabilities to the appropriate communities.

MSEL plays a vital role in nanometrology work at NIST with efforts in four of the seven NNI Program Component Areas — *Instrumentation Research*; *Metrology and Standards for Nanotechnology*; *Nanomaterials*; *Nanomanufacturing*; and *Fundamental Nanoscale Phenomena and Processes*. Innovative projects across MSEL are defining and addressing the forefront research issues in these areas.

Instrumentation Research, Metrology and Standards for Nanotechnology

R&D pertaining to the tools needed to advance nanotechnology research and commercialization. The design, development, and fabrication of nanodevices will require nanomechanical measurements that are rapid, accurate, predictive, well-understood and representative of a device or system's environment in real time. MSEL is addressing this need by developing instrumentation, methodology, reference specimens and multi-scale modeling approaches to quantitatively measure mechanical properties such as modulus, strength, adhesion, and friction at nanometer-length scales. This year, novel instruments for measuring adhesion and friction forces between surfaces and nanoparticles were developed jointly with industrial partners. Quantitative maps of elastic modulus were obtained by innovative methodologies based on atomic force microscopy and strain-induced elastic buckling instability. To address the need for quantifying measurements made with widely-used commercial nanoindentors and scanned probe microscopy instruments, MSEL is developing reference specimens and SI-traceable force calibration methodology.

Nanomaterials

Research aimed at discovery of novel nanoscale and nanostructured materials and at a comprehensive understanding of the properties of nanomaterials. Among the many classes of nanomaterials, nanotubes have received great attention due to their remarkable physical properties relevant to many applications. In response to needs expressed by industry and other federal agencies, MSEL has embarked on a new effort to develop a suite of metrologies and standards aimed at characterizing key structural features and processing variables of carbon nanotubes. These include dispersion, fractionation, orientation, alignment, and manipulation of individual single-walled nanotubes, all critical to establishing efficient bulk processing schemes to meet the imminent high demand for carbon nanotubes.

Nanomanufacturing

R&D aimed at enabling scaled-up, reliable, cost-effective manufacture of nanoscale materials, structures, devices, and systems. Nanoimprint lithography (NIL) is rapidly emerging as a viable high-throughput technique for producing robust structures with a patterning resolution better than 10 nm. MSEL is developing metrologies that are crucial to advancing NIL as an industrial patterning technology for the electronics, optics, and biotechnology industries. The current focus is on characterizing shape and the fidelity of pattern transfer, two key factors in achieving widespread commercial application of NIL.

Fundamental Nanoscale Phenomena and Processes

Discovery and development of fundamental knowledge pertaining to new phenomena in the physical, biological, and engineering sciences that occur at the nanoscale. The magnetic data storage industry needs the ability to measure and control magnetization on nanometer length scales and nanosecond time scales to meet increasing demands for reduced size and increased speed of devices. MSEL is developing measurement techniques to elucidate the fundamental mechanisms of spin dynamics and damping in magnetic thin films. Work this year has focused on measurements of the effects of interfaces and interface roughness on magnetization dynamics and magnetic characterization of edges in magnetic devices.

Through these and other research activities, MSEL is maintaining its committed leadership in developing the measurement infrastructure for current and future nanotechnology-based applications.

Contacts: Alamgir Karim; Kalman Migler



Reference Specimens for SPM Nanometrology

Engineering of nanomaterials, biomaterials, and organic electronic devices hinges on techniques for imaging complex nanoscale features. In this respect, new Scanned Probe Microscopy (SPM) methods promise mapping of chemical, mechanical, and electro-optical properties, but these techniques generally offer only qualitative information. Our reference specimens, fabricated with a combinatorial design, calibrate image data from emerging SPM methods, thereby advancing these nanometrology tools.

Michael J. Fasolka

A new generation of SPM techniques intend to measure chemical, mechanical, and electro/optical properties on the nanoscale. However, contrast in new SPM images is difficult to quantify since probe fabrication can be inconsistent, and probe/sample interactions are not understood. Our research at the NIST Combinatorial Methods Center (NMC) provides reference specimens for the quantification of next-generation SPM data. Using a gradient combinatorial design, our specimens gauge the quality of custom-made SPM probes and calibrate SPM image contrast through “traditional” surface measurements (e.g., spectroscopy and contact angle).

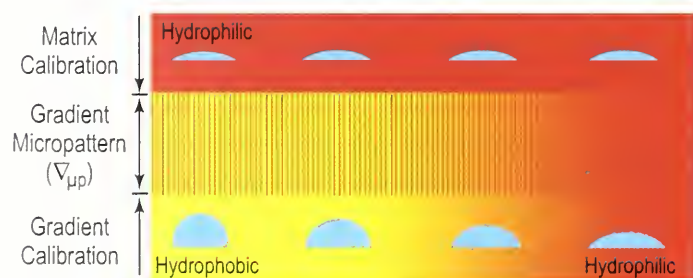


Figure 1: Schematic illustration of the $\nabla\mu_p$ for calibration of chemically sensitive SPM techniques. Blue “droplets” illustrate water contact angle measurement along the calibration strips.

This year, we demonstrated the fabrication and use of a reference substrate that combines patterning of a self-assembled monolayer (SAM) with a surface energy gradient. Our *gradient micropattern* ($\nabla\mu_p$) specimens incorporate a series of micron-scale lines that continuously change in their surface energy compared to a constant matrix. Patterning is achieved via a new vapor-mediated soft lithography of a hydrophobic chlorosilane SAM on SiO_2 (matrix). A subsequent graded UV-Ozone exposure gradually changes the chemistry of the patterned SAM along the specimen from hydrophobic to hydrophilic species. As shown in Figure 1, the specimen design includes two calibration fields, which reflect the changing chemistry of the SAM lines and the constant chemistry

of the matrix. Accordingly, traditional measurements, e.g., water contact angle, along these fields relate the chemical contrast in the $\nabla\mu_p$ to known quantities, e.g., surface energy differences.

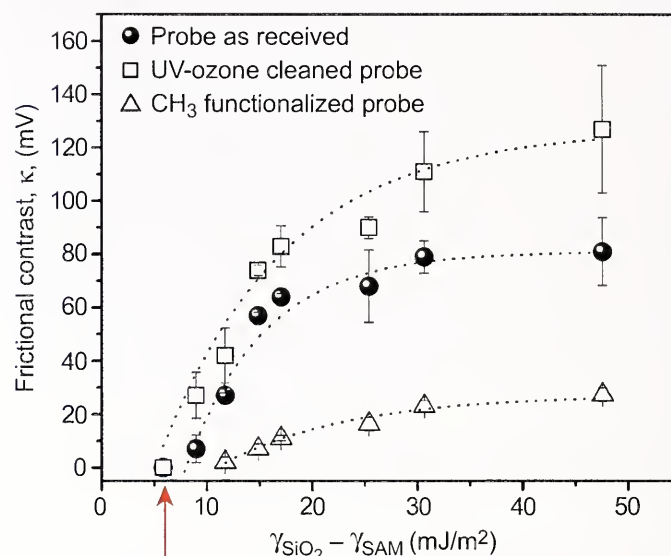


Figure 2: Demonstration of $\nabla\mu_p$ specimen. SPM friction contrast (κ) vs. surface energy (γ) differences obtained with probes of different chemical quality. The red arrow marks the γ -difference sensitivity of a UV-ozone cleaned probe.

Figure 2 demonstrates the utility of the $\nabla\mu_p$ specimen for SPM data calibration. This plot was generated from a series of SPM friction images acquired along the graded pattern. A frictional contrast parameter, κ , which reflects measured friction force differences between the lines and matrix, was extracted from each image. To create a contrast calibration curve, κ is plotted against surface energy data derived from water contact measurements along calibration fields. As shown in Figure 2, the combinatorial $\nabla\mu_p$ provides, in a single specimen, a full-spectrum relationship between SPM friction force and surface energy. As shown through the three curves, the specimen also enables direct comparison between different probe functionalization strategies. Moreover, the curves illuminate the minimum γ -difference detectable by a given probe (where $\kappa \rightarrow 0$), i.e., its chemical sensitivity.

Our fabrication route for the $\nabla\mu_p$, and its use as a reference specimen for emerging SPM techniques, is the subject of an article published in *Nanoletters* (2005, ASAP).

Contributors and Collaborators

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Nanotube Processing and Characterization

Single-wall carbon nanotubes (SWNTs) exhibit remarkable physical properties, and there is considerable interest in using them as nanoscale building blocks for a new generation of applications. Despite this promise, fundamental issues related to the dispersion, fractionation, orientation, and manipulation of individual single-walled carbon nanotubes remain unresolved, and efficient bulk processing schemes do not exist. We are working at the scientific front of this rapidly emerging field to establish research protocols that will help ensure that this new technology progresses as quickly and efficiently as possible, but with uniformly high standards.

Barry J. Bauer, Kalman Migler, and Erik K. Hobbie

Upon their discovery in 1991, carbon nanotubes were recognized as ideal materials for nanotechnology applications. Properties of carbon nanotubes differ vastly depending on their diameter and chirality, and interest in these materials stems from their extraordinary combination of properties: superior thermal conductivity, electrical conductivity, and mechanical strength. Nanotubes are thus attracting great attention for emerging technologies such as bio-chemical sensors, next generation displays, and nano-electronics. Regardless of the ultimate applications, nanotubes clearly represent the most important new class of materials in the past 15 years.

However, application development is plagued by inconsistent sample quality, compounded by a lack of consensus on material characterization methods and by

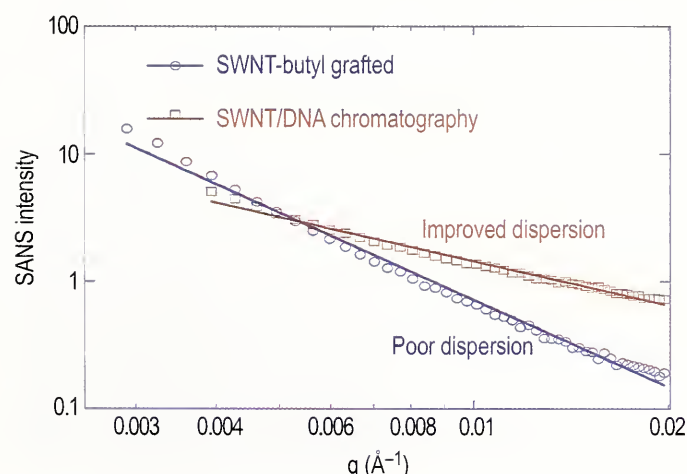


Figure 1: Measured SANS profiles obtained for two different SWNT dispersion chemistries, showing how DNA wrapping provides superior dispersion to other methods, such as chemical functionalization.

poor measurement reproducibility. The quality problems plaguing the nanotube community were described in a recent news article in *Nature* which stated, “the situation will not improve until an external body introduces standards that suppliers can follow.” Few people were surprised by the conclusion of the recent workshop: NIST must take the lead in a quantitative nanotube metrology that will allow suppliers and customers to develop standards for the developing industry.

The Nanotube Processing and Characterization Project within the Polymers Division is actively engaged in this effort. As a starting point, we are currently using small-angle neutron scattering (SANS) to quantify the degree of SWNT dispersion using a variety of dispersion chemistries (Figure 1) and, in doing so, have identified DNA wrapping as desirable for the purpose of fractionating SWNTs by length, diameter, chirality, and band structure.

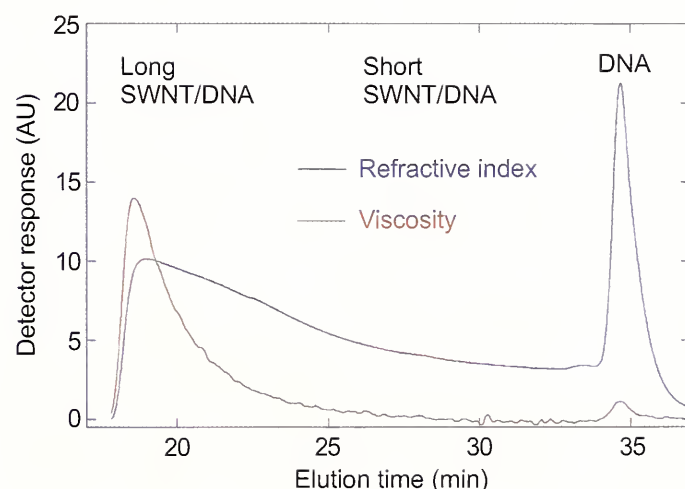


Figure 2: Refractive index and viscosity as a function of elution time in a size-exclusion chromatograph from DNA wrapped SWNTs, showing clear separation by length.

Taking this one step further, we have begun using size-exclusion and ion-exchange chromatography to sort SWNTs by length and chirality (Figure 2). Following the protocol pioneered by DuPont researchers, we are producing ultra clean SWNT fractions that will be characterized with a broad suite of NIST metrologies. These results will in turn be used to establish universal scientific standards for SWNT purity and dispersion.

Contributors and Collaborators

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Combinatorial Adhesion and Mechanical Properties



Traditional methods for evaluating the engineering properties of polymers are time-consuming and inherently single specimen tests. Current market drivers increasingly demand rapid measurement platforms in order to keep pace with competition in the global marketplace. In this project, we are delivering innovative combinatorial and high-throughput (C&HT) tools for the physical testing of materials, built around measurement platforms in the NIST Combinatorial Methods Center (NCMC).

Christopher M. Stafford

Our current C&HT efforts in this project are concentrated in two main areas: buckling mechanics for thin film mechanical measurements and adhesion testing platforms for probing interfacial adhesion and fracture. Here, we highlight: (1) the inversion of our buckling-based metrology to study the mechanical response of soft polymer gels, (2) the application of finite element analysis to study buckling in multilayer geometries, and (3) the implementation of our combinatorial edge delamination test to study the interfacial adhesion strength of epoxy films.

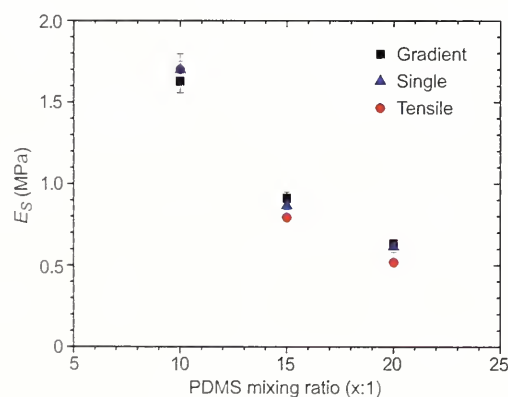


Figure 1: Elastic modulus of model PDMS gels measured via buckling (■ — gradient modulus specimen, ▲ — single specimens) and via tensile test (●).

This year, we applied our buckling-based metrology^[1] to measure the elastic modulus of soft-polymer gels. Elastic modulus is an important design criterion in soft polymer gels for biomedical applications since it impacts critical properties such as adhesion, swelling, and cell proliferation and growth. Leveraging our C&HT buckling-based metrology, we can rapidly assess the elastic modulus of polymer gels by inverting the experimental design: the buckling of a sensor film of known modulus and thickness reports the elastic modulus of the substrate, E_s . Figure 1 illustrates the accuracy of our approach as compared to traditional tensile tests on the same material. One advantage

of our buckling-based technique is that a “modulus map” can be constructed by measuring the buckling wavelength as a function of spatial position.

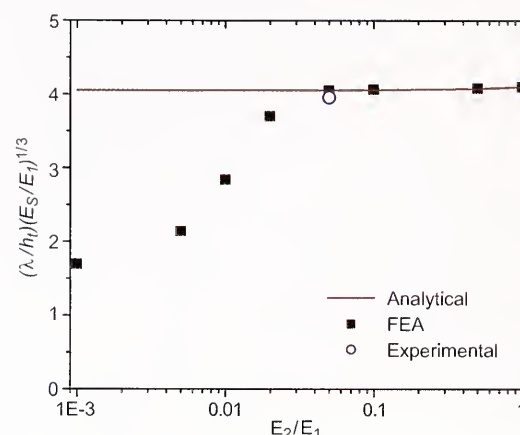


Figure 2: Normalized wavelength versus modulus ratio of a tri-layer thin film. E_2 and E_1 are the moduli of the soft and stiff layer, respectively. The solid line is the analytical solution.

In addition to our experimental efforts, we are also utilizing finite element analysis (FEA) to help guide experimental design in our buckling-based metrology by verifying the validity of available analytical solutions when applied to more complex specimen geometries. For example, we examine a composite film consisting of a soft layer confined between two stiff layers. In Figure 2, FEA reveals a critical modulus ratio below which shear deformation becomes significant, thus the standard analytical solution can no longer be applied to measurements in this regime.

As part of the NCMC, we have launched a Focus Project aimed at developing a C&HT measurement platform for testing interfacial adhesion and fracture in thermally cured epoxy materials. This method is based on the modified edge-lift-off test.^[2] In this Focus Project, we are building capabilities to evaluate the governing parameters for interfacial delamination and reliability by fabricating suitable gradient libraries in composition, thickness, temperature, and applied stress. Industrial sponsors for this Focus Project are ICI National Starch and Intel Corporation.

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Contributors and Collaborators

M.Y.M. Chiang, S. Guo, J.H. Kim, E.A. Wilder, W. Zhang (Polymers Division, NIST); Daisuke Kawaguchi (Nagoya University); Gareth Royston (University of Sheffield)

Soft Nanomanufacturing

Nanomanufacturing is widely noted as a central challenge of nanotechnology. In the realm of soft materials and suspended particles, it is necessary to design particle interactions, manipulate self-assembly processes, and measure what is produced. Guided by theoretical simulations, we are therefore developing high-throughput microfluidic methods for particle characterization, processing, assembly, and on-chip quality control.

Steven D. Hudson

The intricacy of biological systems inspires the design of artificial systems that also function through dynamic self-assembly and *in-situ* monitoring and self-correction.

Our industrial partners identified measurement of interfacial tension as a first hurdle for high-throughput microfluidic fluids analysis. Particle processing and assembly methods represent the next hurdle. In this project, high-throughput tools are developed for these purposes, and theoretical simulations identify particle arrangements whose dynamic assembly and disassembly is promising for sensor applications.

High-throughput measurement of drop shape by image analysis represents the cornerstone of an instrument, developed in collaboration with industrial sponsors, that determines interfacial tension between fluids. The measurement principle is simple and robust — drops are stretched by known viscous forces as they traverse a constriction in the channel. The computer controlled system tracks drop position and deformation more than one hundred times a second.

However, systems that count, isolate, and direct the assembly of particles must operate more efficiently to enable internal feedback mechanisms. Therefore, for

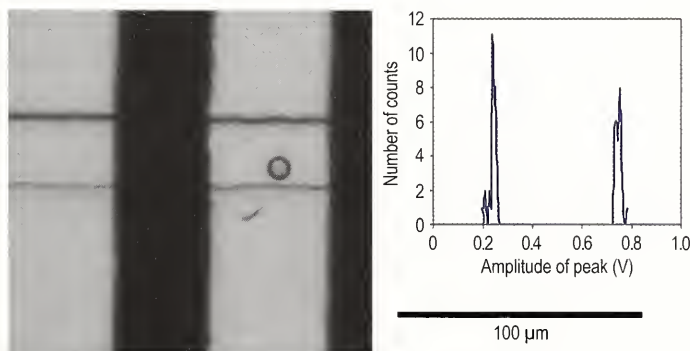


Figure 1: *Inline particle characterization and counting. In the image, a polystyrene particle is seen passing electrodes (dark). At right is shown a bimodal size distribution of liquid drops produced at a T-junction upstream.*

assembly applications, image analysis was replaced by embedded electronic sensors that detect the presence of a particle and its size (Figure 1). This electronic signal activates a valve to isolate a set of particles. Electronic detection is further advantageous because it is readily scalable to smaller particles. In comparison to previous systems, the valves we have developed are also advantageous, since they are not limited to shallow channel profiles.



Figure 2: *Tubular structures (right) arise from the simulated organization of triangular arrangements of dipole particles, shown schematically at left.*

High-throughput sensing and processing methods require precision flow design and control, such as we demonstrated and reported previously by a microfluidic analog of the four-roll mill. Advancing beyond, we developed a framework for generating chaotic flow in microchannels (described in a separate highlight).

Theoretical simulations probe the organization of geometrically and electrostatically asymmetric target particle arrangements (Figure 2). These demonstrate the relationship between particle symmetry and organized structure. Depending on this symmetry, the assemblies exhibit filaments, sheets, tubes and icosahedra. Whereas ordinary phase separation is driven by attractive and repulsive interactions, self-assembly of more complex and finite-sized structures requires directional interactions.

Of consequence for sensor applications, organization kinetics were also investigated. In particular, nucleating agents were found to control the kinetics of assembly and, in polymorphic systems, to specify unique structure.

Contributors and Collaborators

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Defects in Polymer Nanostructures

Nanostructured materials create new and unique functionality through the accurate placement, precise shaping, and chemical modification of nanometer scale patterns. Such materials are to be the basis of a wide range of emerging nanotechnologies that span optics, data storage, and biomembranes. In each of these applications, defects in pattern placement, shape, and chemical composition can compromise device functionality. The rapid development of these technologies is currently offset by a lack of quantitative characterizations of critical defects. We have initiated this project to develop metrologies for characterizing critical defects, such as loss of long-range order, in nanostructured materials.

Ronald L. Jones and Alamgir Karim

The optical, magnetic, and electronic properties of a film or surface are dramatically changed by the inclusion and placement of nanometer-scale patterns. The capability to adjust material properties in this manner is central to the development of sub-wavelength optics, high selectivity biomembranes, nanoparticle synthesis, and ultrahigh capacity data storage. In each of these applications, variations in pattern shape and placement can drastically alter functionality and device viability.

Fabrication of nanostructured surfaces is performed through a wide range of patterning platforms. While photolithographic techniques are traditional routes toward precise patterning, the high cost and complexity of patterning at nanometer length scales has spawned a variety of alternative techniques such as nanoimprint lithography (NIL), self-assembly, and templated self-assembly. Each fabrication technique strives against a common set of critical defects such as variation in pattern placement, chemical uniformity across the pattern cross section, and precision in pattern shape.

To address the needs of this emerging technological area, we have initiated a new program to develop metrologies for long-range order, a critical parameter in optical and data storage applications. Currently, long-range order is quantified from Fourier transforms of real-space microscopy images. However, the disparity in the pattern length scale (~ 10 nm) and the length scale of ordering (~ 100 μm) challenges the measurement range of existing techniques based on scanning electron and scanning probe microscopies. Visible light probes are often complicated by complex interactions with nanometer scale features.

Using small angle x-ray scattering (SAXS), we are developing quantitative descriptions of long-range order, grain size, and pattern shape in hexagonally arrayed cylinders produced on silicon substrates using both nanoimprint lithography (NIL) and self-assembled block copolymers (BCP).

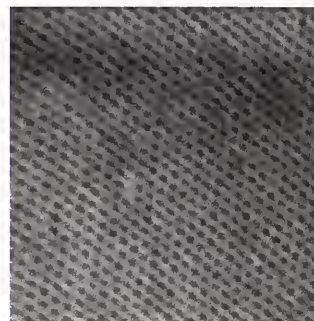


Figure 1: Scanning electron microscopy image showing a regular array of hexagonally packed columns formed in silicon oxide.

For each method of pattern formation, long-range order results in a characteristic diffraction pattern. However, the occurrence of a hexagonal diffraction pattern from the NIL pattern indicates a single crystal spanning the entire 150×150 μm beam spot, while the BCP film consists of multiple, randomly oriented crystals. In both cases, systematic errors in the placement of the patterns on the lattice create a characteristic decay in the intensity as a function of the distance from the beam center.

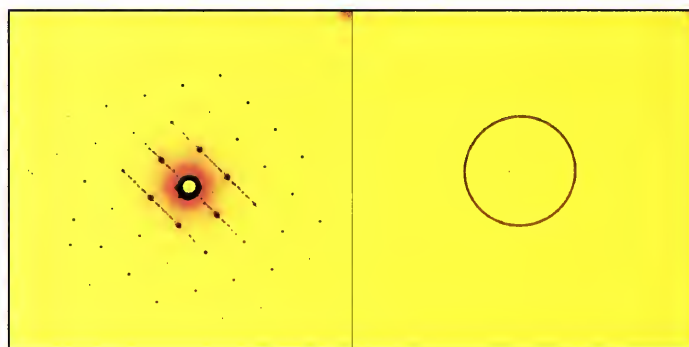


Figure 2: SAXS data from arrays of hexagonally packed columns formed by NIL (left) and self assembly (right).

In addition to developing metrologies for long-range order, we continue to develop a suite of metrologies that address critical needs in a wide range of nanostructured materials applications. These include nanostructured surfaces for adhesion and wettability, as well as nanostructured materials designed for unique electro-optical and magnetic properties.

Contributors and Collaborators

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Critical Dimension Small Angle X-Ray Scattering

The feature size in microelectronic circuitry is ever decreasing and now approaches the scale of nanometers. This creates a need for new metrologies capable of non-destructive measurements of small features with sub-nm precision. NIST has led the effort in developing small angle x-ray scattering to address this need. This x-ray based metrology has been included in the ITRS roadmap as a potential metrological solution for future generation microelectronics fabrication. Other applications of this technique in areas such as nano-rheology and nanofabrication are being explored.

Wen-li Wu and Ronald L. Jones

The demand for increasing computer speed and decreasing power consumption continues to shrink the dimensions of individual circuitry components toward the scale of nanometers. When the smallest, or “critical”, dimensions are < 40 nm, the acceptable tolerance will be < 1 nm. This creates significant challenges for measurements based on electron microscopy and light scatterometry. Device viability also requires the measurement be non-destructive. In addition, the continuing development of new materials for extreme ultraviolet photoresists, nanoporous low-k dielectrics, and metallic interconnects all require high-precision dimensional measurements for process development and optimization.

To address industrial needs, we are developing a high-precision x-ray based metrology termed Critical Dimension Small Angle X-ray Scattering (CD-SAXS). This technique is capable of non-destructive measurements of test patterns routinely used by microelectronic industries to monitor their fabrication process. A collimated monochromatic x-ray beam of sub-Å wavelength is used to measure the pattern dimensions on a substrate in transmission mode. CD-SAXS has previously demonstrated a capability for sub-nm precision for periodicity and line width measurements.

This year, we have extended the capabilities to provide more detailed quantifications of the pattern cross section. This includes both basic dimensions, such as pattern height and sidewall angle, as well as the depth profile of the sidewall damage of nano-patterned low-k dielectrics. The capability to provide basic dimensions is complementary to existing analyses provided by SEM, however CD-SAXS offers significant advantages in its non-destructive capability. In contrast to visible light scatterometry, detailed information on

refractive indices and composition of the pattern are not required for data reduction. These capabilities and the ability to measure patterns approaching dimensions of 10 nm have led to the inclusion of CD-SAXS on the International Technology Roadmap for Semiconductors (ITRS) as a potential metrology for the 45 nm technology node and beyond.

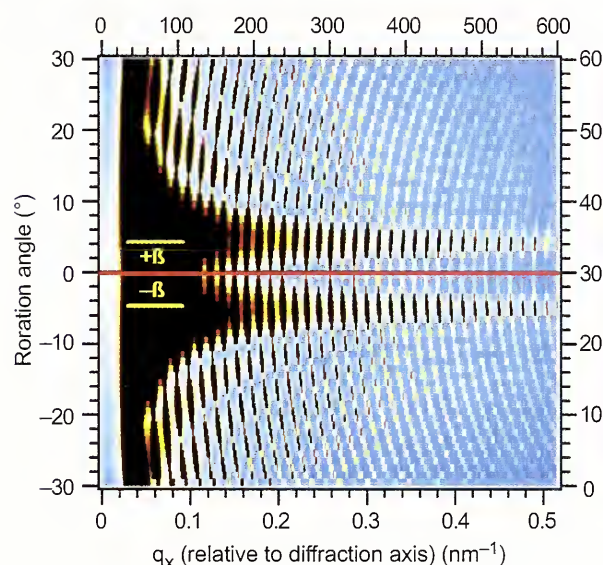


Figure 1: Diffraction patterns collected over a range of sample rotation angles. The distance between the pronounced horizontal ridges provides the sidewall angles β , while the relative intensity and placement of the other diffraction spots provide periodicity, line width, and line height. [$q_x = 4 \pi \sin(\theta/2)/\lambda$, where θ is the angle relative to the diffraction axis and λ is the wavelength of the radiation.]

So far, all CD-SAXS measurements have been carried out at the Advanced Photon Source of Argonne National Laboratory. As an important step in demonstrating the potential of technology transfer, we are constructing the world's first laboratory based CD-SAXS instrument. When completed, this instrument will serve as a prototype for lab-based tool development as well as a world-class metrology tool for nanotechnology research.

Future efforts will develop capabilities for quantifying defects and features with complex shapes such as vias or contact holes. In addition, we will continue to expand efforts in supporting other nanofabrication technologies such as those based on nanoimprint and self assembly.

Contributors and Collaborators

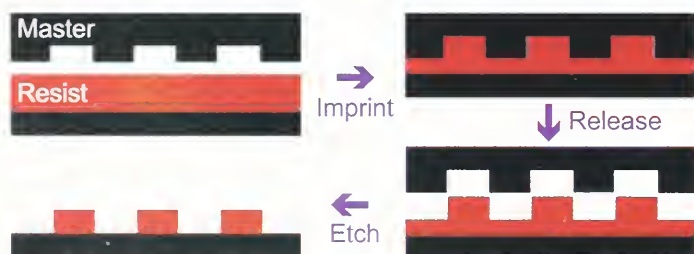
C. Soles, H. Lee, H. Ro, E. Lin (Polymers Division, NIST); K. Choi (Intel); D. Casa, S. Weigand, D. Keane (Argonne National Laboratory); Q. Lin (IBM)

Nanoimprint Lithography

Nanoimprint lithography (NIL) is emerging as a viable next generation lithography with high throughput and a patterning resolution better than 10 nm. However, wide-spread availability of such small nanoscale patterns introduces new metrology challenges as the ability to pattern now surpasses the capability to measure, quantify, or evaluate the material properties in these nanoscale features. We develop high-resolution metrologies to augment and advance NIL technology, with current focus on characterizing shape and the fidelity of pattern transfer.

Christopher L. Soles and Ronald L. Jones

Nanoimprint lithography (NIL) is a conceptually simple process whereby nanoscale patterns are written once into a master, typically Si, quartz, or some other hard material, using a high resolution but slow patterning technology such as e-beam lithography. This master can be rapidly and repeatedly replicated by stamping it into a softer resist film. This imprint replication technique is a cost-effective way to combine the high-resolution patterning of e-beam lithography with the high throughput of a stamping process.

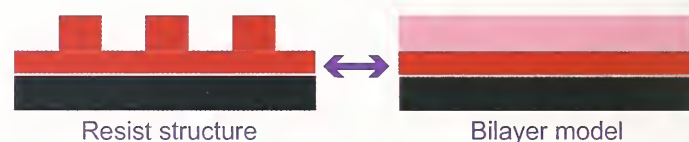


NIL holds great promise in semiconductor fabrication. The high resolution and low cost of ownership make NIL attractive in comparison to expensive next-generation optical lithography tools. However, over the past few years, the interest in NIL has dramatically expanded beyond the realm of traditional CMOS applications. NIL-based solutions are being implemented for optical communications, memory, displays, and biotechnology. Because of these emerging niche applications, NIL is quickly becoming a widely used and versatile nanofabrication tool.

Our objective is to develop metrologies that are crucial to advancing NIL as an industrially viable patterning technology. Initial efforts have focused on developing and applying very accurate pattern-shape measurements. Critical dimension small angle x-ray scattering (CD-SAXS) is a transmission x-ray scattering technique that can quantify the pattern pitch and

cross-section (height, width, side-wall angle) with nm resolution. Likewise, specular x-ray reflectivity (SXR) was introduced to quantify the pattern cross-section and the residual layer thickness with nm resolution. In turn, these accurate shape metrologies enable quantitative studies of imprint resolution and the stability of nanoscale imprinted patterns.

Using CD-SAXS, we demonstrated the fidelity of pattern transfer concept. The pattern cross-sections in the master and the imprint were independently characterized and then compared, to quantify how well the resist material fills and replicates the features of the master. Varying the imprint temperature, pressure, time, and the molecular mass of the imprint material impacts the fidelity of pattern transfer process. We also tracked the *in-situ* evolution of the cross-section while the patterns were annealed close to their glass transition. Rather than a viscous decay, the patterns decreased in height much faster than they broadened in width, owing to the residual stresses in the structures induced by the imprinting procedure. These residual stresses appear to increase with molecular mass, leading to faster rates of pattern decay in higher molecular mass resists.



SXR was used to quantify the residual layer thickness, pattern height, and the relative line shape cross-section. The residual layer is the thin layer of resist that the master is unable to fully displace as it is pressed into the resist film. Precise knowledge of the residual thickness is critical for subsequent etching processes. The key to this measurement is that the x-rays average density over length scales larger than the sub- μm dimensions of the patterns. This leads to the bilayer equivalency model shown above where the patterns can be modeled as a uniform layer of reduced density to extract pattern height and residual layer thickness with nm precision. Like CD-SAXS, SXR quantitatively compares the imprint and the mold to evaluate the fidelity of pattern transfer.

Contributors and Collaborators

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Materials for Electronics

The U.S. electronics industry faces strong international competition in the manufacture of smaller, faster, more functional, and more reliable products. Many critical challenges facing the industry require the continual development of advanced materials and processes. The NIST Materials Science and Engineering Laboratory (MSEL) works closely with U.S. industry, covering a broad spectrum of sectors including semiconductor manufacturing, device components, packaging, data storage, and assembly, as well as complementary and emerging areas such as optoelectronics and organic electronics. MSEL has a multidivisional approach, committed to addressing the most critical materials measurement and standards issues for electronic materials. Our vision is to be the key resource within the Federal Government for materials metrology development and will be realized through the following objectives:

- Develop and deliver standard measurements and data for thin film and nanoscale structures;
- Develop advanced measurement methods needed by industry to address new problems that arise with the development of new materials;
- Develop and apply *in situ* as well as real-time, factory floor measurements for materials and devices having micrometer to nanometer scale dimensions;
- Develop combinatorial material methodologies for the rapid optimization of industrially important electronic and photonic materials;
- Provide fundamental understanding of the divergence of thin film and nanoscale material properties from their bulk values;
- Provide fundamental understanding, including first principles modeling, of materials needed for future nanoelectronic devices.

The NIST/MSEL program consists of projects led by the Metallurgy, Polymers, Materials Reliability, and Ceramics Divisions. These projects are conducted in collaboration with partners from industrial consortia (e.g., SEMATECH), individual companies, academia, and other government agencies. The program is strongly coupled with other microelectronics programs within the government such as the National Semiconductor Metrology Program (NSMP). Materials metrology needs are also identified through the International Technology Roadmap for Semiconductors (ITRS), the International Packaging Consortium (IPC) Roadmap, the IPC Lead-free Solder Roadmap, the National Electronics Manufacturing Initiative (NEMI) Roadmap, the Optoelectronics Industry Development Association (OIDA) Roadmap, and the National Magnetic Data Storage Industry Consortium (NSIC) Roadmap.

MSEL researchers from each division have made substantial contributions to the most pressing technical challenges facing industry, from new fabrication methods and advanced materials in the semiconductor industry, to low-cost organic electronics, and to novel classes of electronic ceramics. Below are just a few examples of MSEL contributions over the past year.

Advanced Gate Dielectrics

To enable further device scaling, the capacitive equivalent thickness (CET) of the gate stack thickness must be 0.5 nm to 1.0 nm. This is not achievable with existing SiO₂/polycrystalline Si gate stacks. High dielectric constant gate insulators are needed to replace SiO₂, and metal gate electrodes are needed to replace polycrystalline Si. Given the large number of possible materials choices for the gate dielectric/substrate and gate dielectric/metal gate electrode interfaces, the MSEL Ceramics Division is establishing a dedicated combinatorial film deposition facility to study the complex interfacial interactions. This same methodology is applicable to a wide variety of problems in the electronic materials field.

Advanced Lithography

Lithography is the key enabling technology for the fabrication of advanced integrated circuits. As feature sizes decrease to sub-65 nm length scales, challenges arise because the image resolution and the thickness of the imaging layer approach the dimensions of the polymers used in the photoresist film. Unique high-spatial resolution measurements are developed to identify the limits of materials and processes for the development of photoresists for next-generation lithography.

Advanced Metallization

As the dimensions of copper metallization interconnects on microelectronic chips decrease below 100 nm, control of electrical resistivity becomes critical. The MSEL Metallurgy Division is developing seedless deposition methods that will simplify thin-film processing and result in film growth modes that increase trench filling, thus lowering interconnect resistivity.

Mechanical Reliability of Microchips

One of the important ITRS challenges is to achieve effective control of the failure mechanisms affecting chip reliability. Detection and characterization methods for dimensionally constrained materials will be critical to the attainment of this objective. Scientists in the MSEL Materials Reliability Division are addressing this issue by focusing on electrical methods capable of determining the thermal fatigue lifetime and mechanical strength of patterned metal film interconnects essential to microchips.

Contact: Eric K. Lin

Polymer Photoresists for Nanolithography

Photolithography, the process used to fabricate integrated circuits, is the key enabler and driver for the microelectronics industry. As lithographic feature sizes decrease to the sub 65 nm length scale, challenges arise because both the image resolution and the thickness of the imaging layer approach the macromolecular dimensions characteristic of the polymers used in the photoresist film. Unique high-spatial resolution measurements are developed to reveal limits on materials and processes that challenge the development of photoresists for next-generation sub 65 nm lithography.

Vivek M. Prabhu

Photolithography is the driving technology used by the microelectronics industry to fabricate integrated circuits with ever decreasing sizes. In addition, this fabrication technology is rapidly being adopted in emerging areas in optoelectronics and biotechnology requiring the rapid manufacture of nanoscale structures. In this process, a designed pattern is transferred to the silicon substrate by altering the solubility of areas of a polymer-based photoresist thin film through an acid-catalyzed deprotection reaction after exposure to radiation through a mask (Figure 1). To fabricate smaller features, next-generation photolithography will be processed with shorter wavelengths of light requiring photoresist films less than 100 nm thick and dimensional control to within 2 nm.

To advance this key fabrication technology, we work closely with industrial collaborators to develop and apply high-spatial resolution and chemically specific measurements to understand changes in material properties, interfacial behavior, and process kinetics that can significantly affect the patterning process at nanometer scales.

This year, we initiated two new collaborations. With SEMATECH, we are determining the materials sources of line-edge roughness in model 193-nm photoresists. With the Intel Corporation, we are investigating the effect of extreme ultraviolet (EUV) exposure on pattern resolution of model EUV photoresist materials. With these partners, we continue to provide new insight and detail into the complex physico-chemical processes used in advanced chemically amplified photoresists. These methods include x-ray and neutron reflectivity (XR, NR), small angle neutron scattering (SANS), near-edge x-ray absorption fine structure (NEXAFS) spectroscopy, combinatorial methods, solid state nuclear magnetic

resonance (NMR)/spectroscopy, quartz crystal microbalance (QCM), Fourier transform infrared spectroscopy (FTIR), fluorescence correlation spectroscopy (FCS), and atomic force microscopy (AFM).

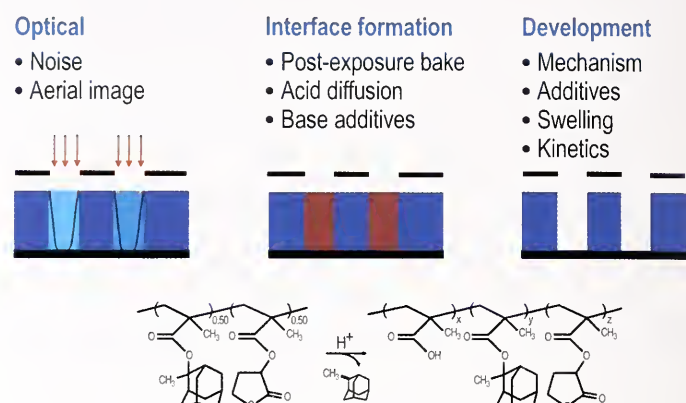


Figure 1: Key lithographic process steps; each step requires an interdisciplinary array of experimental techniques to measure the polymer chemistry and physics in thin films. A model 193-nm resist under investigation is shown with the acid-catalyzed deprotection reaction.

Photoresists are multi-component mixtures that require dispersion of additives, controlled transport properties during the interface formation, and controlled dissolution behavior. The fidelity of pattern formation relies on the materials characteristics. We examine the influence of copolymer compositions, molecular mass, and photoacid generator additive size to determine the root causes of image quality by highlighting the fundamental polymer physics and chemistry. In addition, our collaborators test our hypotheses using 193-nm and EUV lithographic production tools.

Accomplishments for this past year include: quantification of the developer profile in ultrathin films by NR and QCM; quantification of the deprotection reaction kinetics and photoacid-reaction diffusion deprotection front for resolution and roughness fundamentals by combined NR and FTIR; photoacid generator miscibility and dispersion in complex photoresist co- and ter-polymers by NMR; and aqueous immersion dependence on photoresist component leaching by NEXAFS.

Contributors and Collaborators

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Organic Electronics

Organic electronics has dramatically emerged in recent years as an increasingly important technology encompassing a wide array of devices and applications including embedded passive devices, flexible displays, and sensors. Device performance, stability, and function critically depend upon charge transport and material interaction at the interfaces of disparate materials. We develop and apply nondestructive measurement methods to characterize the electronic and interfacial structure of organic electronics materials with respect to processing methods, processing variables, and materials characteristics.

Eric K. Lin and Dean M. DeLongchamp

Organic electronic devices are projected to revolutionize new types of integrated circuits through new applications that take advantage of low-cost, high-volume manufacturing, nontraditional substrates, and designed functionality. The current state of organic electronics is slowed by the concurrent development of multiple material platforms and processes and a lack of measurement standardization between laboratories. A critical need exists for new diagnostic probes, tools, and methods to address these technological challenges.

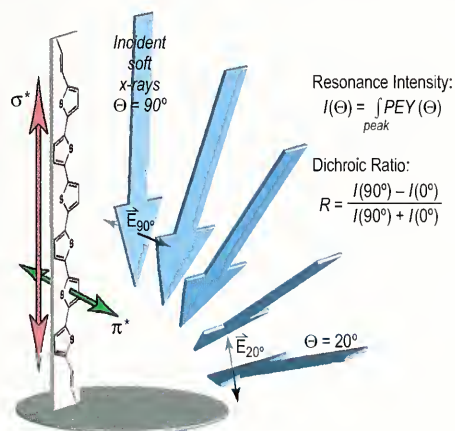


Figure 1: Schematic of the geometry of near-edge x-ray absorption fine structure (NEXAFS) spectroscopy for the determination of the orientation of an oligothiophene organic semiconductor synthesized by the University of California–Berkeley.

Organic electronics presents different measurement challenges from those identified for inorganic devices. We are developing an integrated suite of metrologies to correlate device performance with the structure, properties, and chemistry of materials and interfaces. We apply new measurement methods to provide the data and insight needed for the rational and directed development of emerging materials and processes. Studies include AC measurements of organic semiconductor thin films,

the influence of surface modification layers on device performance, and the evaluation of moisture barrier layers for device encapsulation.

This year, near-edge x-ray absorption fine structure (NEXAFS) spectroscopy was applied to several classes of organic electronics materials to investigate the electronic structure, chemistry, and orientation of these molecules near a supporting substrate. NEXAFS spectroscopy was used successfully to quantify the simultaneous chemical conversion, molecular ordering, and defect formation of soluble oligothiophene precursor films for application in organic field effect transistors. Variations in field-effect hole mobility with thermal processing were directly correlated to the orientation and distribution of molecules within 3 nm to 20 nm thick films.

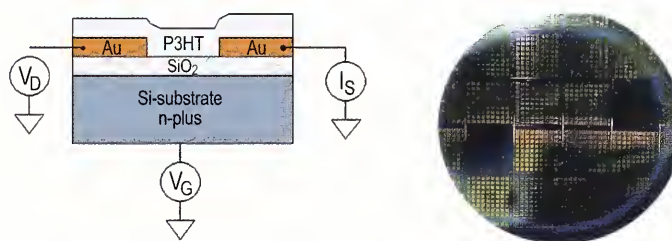


Figure 2: Schematic of an organic field effect transistor (OFET) and a photo of the NIST OFET test bed fabricated onto silicon.

Organic field effect transistor test structures were also designed and fabricated onto silicon wafers with variations in transistor channel length and width. Devices constructed using organic semiconductors such as poly(3-hexyl thiophene) (P3HT) were tested for their electrical characteristics such as the field effect hole mobility, on/off ratios, and threshold mobilities. Variations in mobility, for example, are observed with changes in processing variables such as annealing temperature and casting solvent. Correlations are found between device performance and the microstructure of P3HT as quantified by NEXAFS, optical ellipsometry, and FTIR spectroscopy.

Contributors and Collaborators

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Nanoporous Low-k Dielectric Constant Thin Films

NIST provides the semiconductor industry with unique on-wafer measurements of the physical and structural properties of nanoporous thin films. Several complementary experimental techniques are used to measure the pore and matrix morphology of candidate materials. The data are used by industry to select candidate low-k materials. Measurement methods such as x-ray porosimetry and small angle x-ray scattering are developed that may be transferred to industrial laboratories. Methods are being developed to measure patterned low-k samples and to assess the extent of structure modification caused by plasma etch.

Eric K. Lin and Wen-li Wu

Future generations of integrated circuits will require porous low-k interlayer dielectric materials to address issues with power consumption, signal propagation delays, and crosstalk that decrease device performance. The introduction of nanometer scale pores into a solid film lowers its effective dielectric constant. However, increasing porosity adversely affects other important quantities such as the physical strength needed to survive chemical mechanical polishing steps and barrier properties to contaminants such as water. These effects pose severe challenges to the integration of porous dielectrics into the device structure.

There is a need for nondestructive, on-wafer characterization of nanoporous thin films. Parameters such as the pore size distribution, wall density, porosity, film uniformity, elemental composition, coefficient of thermal expansion, and film density are needed to evaluate candidate low-k materials. NIST continues to develop low-k characterization methods using a combination of complementary measurement methods including small angle neutron and x-ray scattering (SANS, SAXS), high-resolution x-ray reflectivity (XR), x-ray porosimetry (XRP), SANS porosimetry, and ion scattering. To facilitate the transfer of measurement expertise, a recommended practice guide for XRP is available for interested researchers.

In collaboration with industrial and university partners, we have applied existing methods to new low-k materials and developed new methods to address upcoming integration challenges. A materials database developed in collaboration with SEMATECH is used extensively by SEMATECH and its member companies to help select candidate materials and to optimize integration processing conditions. We address the effects of the ashing/plasma etch process on the low-k

material during pattern transfer. Often surfaces exposed to ashing/plasma densify and lose terminal groups (hydrogen or organic moiety) resulting in an increased moisture adsorption and thus dielectric constant. XR measurements enable quantification of the surface densification or pore collapse in ashing-treated and/or plasma-treated blanket films.

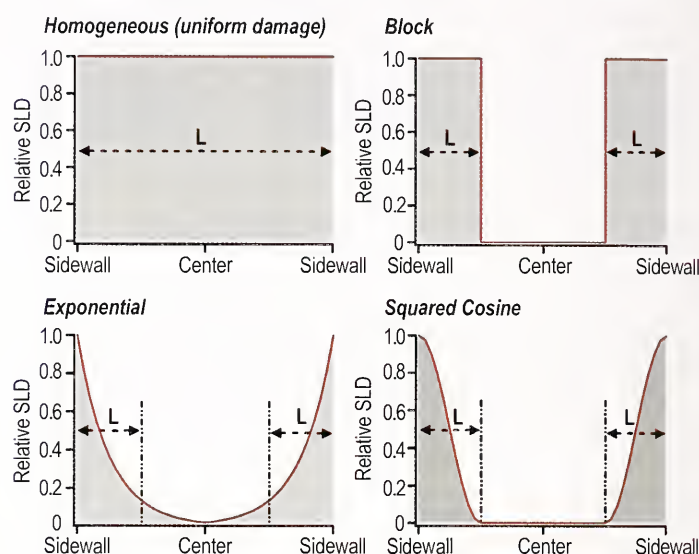


Figure 1: Four models of the damage layer profile plotted as scattering length density (SLD) as a function of position within a line. The matrix has a relative SLD of zero in the above plots.

This year, a new method using SAXS was developed to investigate the effect of plasma etch on patterned low-k films. After the plasma etch process, samples are backfilled with the initial low-k material. Any densification of the sidewall may be observable by x-ray scattering from the cross-section of a patterned nanostructure. This SAXS work was carried out at Argonne National Laboratory using line gratings of low-k material. The resulting data can then be compared with several different scattering models for the densification of the patterned low-k material as shown in Figure 1. Distinctions between models such as these will significantly help semiconductor manufacturers to accelerate the integration of low-k materials into next generation devices.

Contributors and Collaborators

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Advanced Manufacturing Processes

The competitiveness of U.S. manufacturers depends substantially on their ability to create new product concepts and to quickly translate such concepts into manufactured products that meet their customers' increasing expectations of performance, cost, and reliability. This is equally true for well-established "commodity" industries, such as automotive, aerospace, and electronics; for materials suppliers of aluminum, steel, and polymers; and for rapidly growing industries based on nanotechnology and biotechnology. In support of these industries, MSEL is developing robust measurement methods, standards, software, and process and materials data needed for design, monitoring, and control of new and existing materials and their manufacturing processes. The Advanced Manufacturing Processes Program focuses on the following high-impact areas:

- Development of combinatorial and high-throughput methods for developing and characterizing materials ranging from thin films and nanocomposites to micro and macroscale materials structures;
- Automotive industry-targeted R&D for improved measurement methods for sheet metal forming of lightweight metals and for the development of hydrogen storage materials needed for hydrogen-powered vehicles;
- Development of innovative, physics-based process modeling tools for simulating phase transformations and deformation during manufacturing and creation of the databases that support such simulations;
- National traceable standards having a major impact on trade, such as hardness standards for metals and MALDI process standards for polymers; and
- Development of innovative microfluidic testbeds for process design and characterization of polymer formulations.

Our research is conducted in close collaboration with industrial partners, including industrial consortia, and with national standards organizations. These collaborations not only ensure the relevance of our research, but also promote rapid transfer and utilization of our research by our partners. Three projects from the Advanced Manufacturing Methods Program are highlighted below.

NIST Combinatorial Methods Center (NCCM)

The NCCM develops innovative combinatorial and high-throughput (C&HT) measurement techniques and experimental strategies for accelerating the discovery and optimization of complex materials and products, such as polymer coatings and films, structural plastics,

fuels, personal care goods, and adhesives. These C&HT array and gradient methods enable the rapid acquisition and analysis of physical and chemical data from materials libraries, thereby accelerating materials discovery, manufacturing design, and knowledge generation. In 2005, the NCCM Consortium consisted of 19 institutions from industry, government laboratories, and academic groups, which represents a broad cross-section of the chemical and materials research sectors. A growing component of the NIST NCCM program is focused on accelerating the development and understanding of emerging technologies, including nanostructured materials, organic electronics, and biomaterials, and, in particular, on the nanometrology needed for C&HT-based research for these technologies.

Forming of Lightweight Materials

Automotive manufacturing is a materials intensive industry that involves approximately 10 % of the U.S. workforce. In spite of the use of the most advanced, cost-effective technologies, this globally competitive industry has major productivity issues related to materials measurements, materials modeling, and process design. Chief among these is the difficulty of designing stamping dies for sheet metal forming. An ATP-sponsored workshop ("The Road Ahead," June 20–22, 2000) identified problems in the production of working die sets as the main obstacle to reducing the time between accepting a new design and actual production of parts. This is also the largest single cost (besides labor) in car production. Existing finite element models of deformation and the materials measurements and data on which they are based are inadequate to the task of evaluating a die set design: they do not accurately predict the multi-axial hardening, springback, and friction of sheet metal during metal forming processes and, therefore, the stamping dies designed using finite element analyses must be modified through physical prototyping to produce the desired shapes, particularly for high-strength steels and aluminum alloys. To realize the weight savings and increased fuel economy enabled by high-strength steel and aluminum alloys, a whole new level of formability measurement methods, models, and data is needed for accurate die design, backed by a better understanding of the physics behind metal deformation. The MSEL Metallurgy Division is working with the U.S. automakers and their suppliers to fill these needs. A key component of our program is the unique multi-axial deformation measurement facility with which local strains in deformed metal sheet can be measured *in situ*. This facility has enabled NIST to take a key role in developing new methods for

assessing springback, residual stresses, friction between the sheet metal and die during forming, and surface roughening, and in providing benchmark data for international round-robin experiments for finite element code. New techniques for detecting local deformation events at surfaces are providing insights into the physics of deformation and are leading to physics-based constitutive equations.

Hardness Standardization: Rockwell, Vickers, and Knoop

Hardness is the primary test measurement used to determine and specify the mechanical properties of metal products and, as such, determines compliance with customer specifications in the national and international marketplace. The MSEL Metallurgy Division is engaged in developing and maintaining national traceability for hardness measurements and in assisting U.S. industry in making measurements compatible with other countries around the world, enabled through our chairing the ASTM International Committee on Indentation Hardness Testing and heading the U.S. delegation to the ISO Committee on Hardness Testing of Metals, which oversees the development of the organizations' respective hardness programs. Our specific R&D responsibilities include the standardization of the national hardness scales, development of primary reference transfer standards, leadership in national and international standards writing organizations, and interactions and comparisons with U.S. laboratories and the National Metrology Institutes of other countries.

Contact: Michael J. Fasolka



NIST Combinatorial Methods Center Pioneer and Partner in Accelerated Materials Research

Combinatorial and high-throughput (C&HT) methods hold great potential for making materials research more productive, more thorough, and less wasteful. However, significant barriers prevent the widespread adoption of these revolutionary techniques. Through creative, cost-effective measurement solutions, and with an eye towards fruitful collaboration, the NIST Combinatorial Methods Center (NCMC) strives to ease the acquisition of C&HT techniques by the materials research community.

Michael J. Fasolka

The NIST Combinatorial Methods Center is now in its fourth year of service to industry, government laboratories, and academic groups interested in acquiring C&HT capabilities for materials research. In 2005, the NCMC consortium included 19 member institutions (see table), which represent a broad cross-section of the chemical and materials research sectors.

The NCMC fosters wide-spread adaptation of C&HT technologies through two complementary efforts. The first is an extensive research program, centered in the Multivariant Measurement Methods Group of the NIST Polymers Division. Our research provides innovative measurement solutions that serve to accelerate the discovery and optimization of complex products such as polymer coatings and films, structural plastics, fuels, personal care goods and adhesives. Moreover, a growing component of our program aims to speed the development and understanding of emerging technologies including nanostructured materials, nanometrology, organic electronics, and biomaterials. Several of these research directions are highlighted elsewhere in this report, as identified by the NCMC symbol (see top right).

"The coatings industry has been traditionally perceived to react slowly to implementing newer and quantifiable measurement techniques for characterizing structure-property relationships in paints and films. The [NCMC] has pioneered elegant approaches that can significantly reduce experimental time [for] testing coating formulation performance."

— D. Bhattacharya (Eastman Chemical)

In conjunction with its research program, the NCMC conducts an outreach effort to disseminate NIST-developed C&HT methods, assess industry measurement needs, and form a community to advance the field. A key component of NCMC outreach is our series of member workshops. On November 8–9 2004, we hosted our 6th workshop, *NCMC-6: Advanced Materials Forum*. The goal of *NCMC-6* was to gauge

emerging industrial needs for C&HT measurements of materials systems such as biomaterials and organic electronics. Accordingly, *NCMC-6* included plenary symposia outlining engineering issues in these advanced systems, sessions illustrating NIST capabilities in these areas, and a panel discussion aimed at determining new measurements that should be pursued.

In addition, on May 2–3 2005, we hosted *NCMC-7: Adhesion and Mechanical Properties II*. Central to this event was a symposium presenting new NCMC methods for the development and optimization of adhesives. Highlights included a new gradient peel-test for the HT assessment of backed adhesives (e.g., tapes), and approaches for the rapid screening of epoxy formulations. A variation of our buckling technique to measure modulus, useful for evaluating soft systems such as polymer gels, was also described.

"As a member of NCMC, I believe that Procter & Gamble has access to a high-performance work group with expertise in high throughput and combinatorial techniques. The conferences have been particularly valuable for networking with NIST scientists as well as other industrial members of NCMC."

— M. McDonald (Procter and Gamble)

Moreover, this year the NCMC continued community forming activities by organizing several high-profile sessions dedicated to C&HT research at national conferences, including meetings of the American Physical Society, the American Chemical Society, the Materials Research Society, and the Adhesion Society.

"The combinatorial methods program at NIST makes the NCMC critical to any company's development of high-throughput workflows. The import of this effort to industry is clearly indicated by your center's number of industrial members."

— J. Dias (ExxonMobil)

For more information on the NIST Combinatorial Methods Center, please visit <http://www.nist.gov/combi>.

NCMC Members (*New in FY2005):

Air Force Research Lab	Hysitron International
Air Products & Chemicals	Intel
Arkema Inc.	ICI/National Starch & Chemicals
BASF	L'Oreal*
Bayer Polymers	PPG Industries
BP	Procter & Gamble
Dow Chemical Company	Rhodia
Eastman Chemical	Univ. of Southern Mississippi
ExxonMobil Research	Veeco/Digital Instruments
Honeywell International	

Contributors and Collaborators

C.M. Stafford, P.M. McGuigan, K.L. Beers, A. Karim, E.J. Amis (Polymers Division, NIST)

Polymer Formulations: Materials Processing and Characterization on a Chip

We develop high-throughput methods to advance polymer formulations science through the fabrication of microscale instrumentation for measuring physical properties of complex mixtures. Adaptation of microfluidic technology to polymer fluid processing and measurements provides an inexpensive, versatile alternative to the existing paradigm of combinatorial methods. We have built a platform of polymer formulations-related functions based on modified microfluidic device fabrication methods established in our facilities.

Kathryn L. Beers

Microfluidic device fabrication methods previously developed in the Polymers Division enable combinatorial fabrication and characterization of polymer libraries. Recent accomplishments include the integration of multiple functions on a chip for the formulation, mixing, processing, and characterization of polymer particles for evaluation of dental composite materials and the fabrication of gradient polymer brush surfaces for measuring the behavior of stimuli-responsive surfaces.

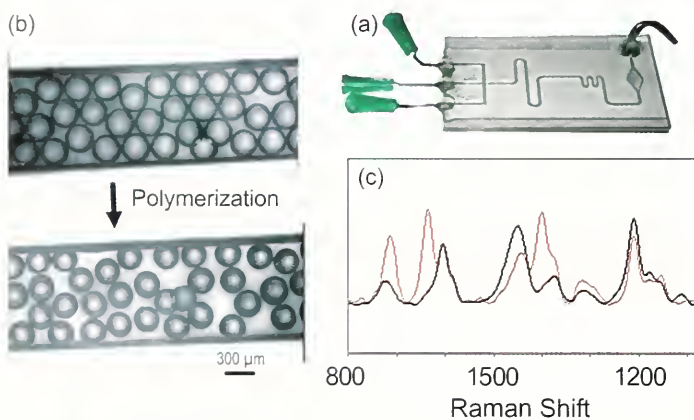


Figure 1: (a) A thiolene microfluidic device used to create, mix, polymerize and characterize monomer droplets. (b) Optical images of monomer droplets and polymer particles. (c) Raman spectra of monomer (red) and polymer (black).

Building on our ability to form organic-phase droplets in thiolene-based microfluidic devices (Figure 1a), we can establish libraries of droplets with systematic composition variations. The droplets are subject to various processes such as mixing and photopolymerization on the chip. Raman spectroscopy on the chip (Figure 1c) and optical imaging (Figure 1b) are used to measure and correlate properties such as monomer composition and conversion to polymer

with shrinkage. The first publication on this work (*Langmuir* **21**, 3629, 2005) was recently profiled in the Research Highlights of *Lab on a Chip*.

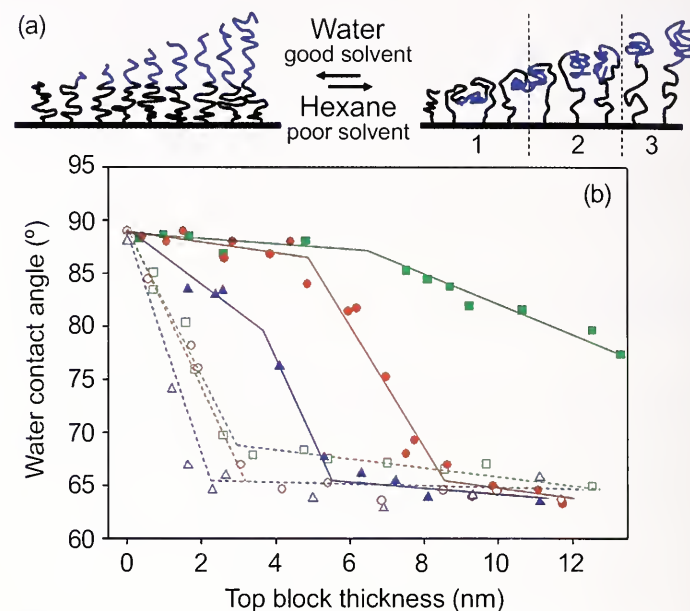


Figure 2: (a) Schematic of amphiphilic block copolymer brush gradients representing the proposed conformation shift in response to good and poor solvents for the top block layer. (b) Water contact angle measurements as a function of top block thickness on three gradients of top block thickness on uniform bottom blocks of three different lengths (blue – 4 nm, red – 10 nm, green – 14 nm) in good (open) and poor (filled) solvents for the top block.

Microchannel confined surface initiated polymerization was used to prepare surfaces with gradients of molecular mass and block and statistical copolymer composition. The block copolymer surfaces were studied for their ability to reorganize at the air/solution interface depending on the nature of the polymer and solvent (Figure 2a). The ability of the surface layer to rearrange was shown to depend on the thickness of both the top and bottom block layers (Figure 2b).

The capabilities for controlled radical polymerization on a chip (CRP Chip) were also extended this year to include block copolymer synthesis and higher-order control of solution compositions. A three-input device was developed, enabling stoichiometric variations in reactions and faster measurement of kinetic behavior (*Macromol. Rapid Commun.* **26**, 1037, 2005).

Contributors and Collaborators

Z.T. Cygan, C. Xu, S. Barnes, T. Wu, A.J. Bur, J.T. Cabral, S.D. Hudson, A.I. Norman, J. Pathak, W. Zhang, M.J. Fasolka, E.J. Amis (Polymers Division, NIST)

Quantitative Polymer Mass Spectrometry

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) is being developed as a method for absolute molecular mass distribution measurement of synthetic polymers. This means determining a comprehensive uncertainty budget for a complex measurement technique that must include both Type A ("random") and Type B ("systematic") uncertainties.

William E. Wallace

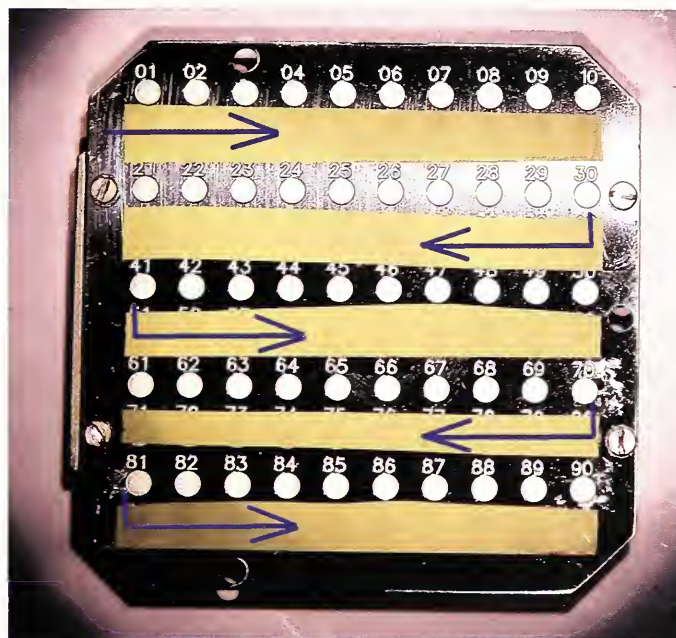
In mass spectrometry, methods exist to calibrate the mass axis with high precision and accuracy. In contrast, the ion-intensity axis is extremely difficult to calibrate. This leads to large uncertainties in quantifying the content of mixtures. This is even true when the mixture is composed solely of different mass oligomers of the same chemical species as in the case of polymer polydispersity. The aim of this project is to calibrate the ion intensity axis. This task has been divided into three parts: sample preparation/ion production, instrument optimization/ion separation, and data analysis/peak integration. Each part is necessary but on its own is not sufficient to guarantee quantitation.

We study the MALDI ion-creation process phenomenologically using combinatorial libraries. The ratio of analyte to matrix is varied along a linear path laid down by nebulizing a continuously varying mixture of two solutions, one analyte+matrix+salt and the other matrix+salt. In our case, the analyte is a mixture of two polymers having different end groups and closely matched molecular mass distributions. The figure on this page shows such a library where the blue arrows indicate a linearly changing analyte:matrix ratio.

To this, we add stochastic-gradient numerical optimization to adjust the instrument parameters at each composition to give a mass spectrum that best matches the known polymerA:polymerB ratio in the analyte. Instrument parameters optimized include laser energy, ion extraction voltage, ion lens voltage, extraction delay time, and detector voltage. Stochastic methods must be used because the data have some measure of Type A random uncertainty (*i.e.*, "noise") to them; therefore, exact values of the function to be optimized are not available.

Finally, to this we add our *MassSpectator* software which ensures unbiased, logically-consistent integration

of the peaks in the (noisy) mass spectrum. A software script has been written around *MassSpectator* that automatically identifies oligomeric series in the mass spectrum and calculates the total amount and the molecular mass moments for each series identified.



An early embodiment of our approach can be found in ASTM Standard Test Method D7134, the first MALDI-TOF-MS method endorsed by ASTM. Working through the Versailles Project on Advanced Materials and Standards (VAMAS), and in close cooperation with our industry and national metrology institute (NMI) colleagues from around the world, an interlaboratory comparison was initiated to understand the nexus of critical measurement factors when performing quantitative polymer mass spectrometry. From the knowledge gained by the interlaboratory comparison, D7134 was written with particular attention paid toward controlling the critical factors.

The MALDI project maintains a vigorous, worldwide outreach program including an online polymer MALDI recipes catalog, annual polymer MS workshops, and the availability of our *MassSpectator* software on the web. For more information on any of these topics please visit our web page at: www.nist.gov/maldi.

Contributors and Collaborators

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Biomaterials

Rapid development of medical technologies depends on the availability of adequate methods to characterize, standardize, control, and mass produce them. To realize this goal, a measurement infrastructure is needed to bridge the gap between the exponentially increasing basic biomedical knowledge and clinical applications. The MSEL Biomaterials Program is a collaborative effort creating a new generation of performance standards and predictive tools targeting the metrology chain for biomedical research.

Today, all areas of materials science confront real systems and processes. In the biomaterials arena, we can no longer advance science by simply studying ideal model systems. We must comprehend complex realistic systems in terms of their structure, function, and dynamics over the size range from nanometers to millimeters. MSEL is uniquely positioned to make a major contribution to the development of measurement infrastructure through three focus areas: *Systems Biology*, *Bioimaging*, and *Nanobiosensing*.

Systems Biology

MSEL research in systems biology focuses on quantifying relationships of systems at the cell, tissue, and organ level. To meet this need, we are developing libraries of reference materials, high-throughput techniques for screening libraries, and informatics approaches for data analysis and interpretation. Physicochemical and biochemical components are organized using patterning, phase separating, and self-assembling processes. Physicochemical components of interest include modulus and surface topography; biochemical components of interest include peptide moieties that interact specifically with cell receptors.

Gradient libraries of tyrosine derivatized polycarbonate blends and fibronectin/poly(hydroethyl-methacrylate) gradients were developed as reference materials for biomaterial research, such that cell responses included changes in geometry, distribution, and proliferation, to assess intercellular communication among osteoblast and fibroblast cells. Complementing these surface studies, we are developing metrologies to establish the relationship between 3D scaffold morphology (i.e., porosity and permeability) and cell response. Studies focused on identifying the relationship between applied macroscopic stresses and local stresses at the cellular level is also underway, which will provide valuable input into development of finite-element models.

Experiments on the mechanical stimulation of tissues and tissue engineered constructs were conducted to understand the role of metrology in diagnostic testing of healthy or disease states. Stress-strain relationships were defined for vascular smooth muscle cells and bovine cardiac tissues. Specialized bioreactors coupled to ultrasound and infra-red spectroscopy were successful in differentiating response among the systems. We have demonstrated that the structure-property relations in healthy tissue of pulmonary arteries, and in tissue that has remodeled in response to the onset of disease, can be assessed using mechanical testing, quantitative ultrasonic characterization, and histology.

Bioimaging

Advances were made in developing and optimizing physical methods and informatics tools to enhance bioimaging and visualization technologies at multiple length scales. With the reduction of background noise, images were obtained using broadband coherent anti-stokes Raman scattering microscopy with a 10-fold increase in signal, and proteins on the surface of polymer blends were differentiated. Optical techniques like OCM and CFM, with spatial resolutions of $\approx 1 \mu\text{m}$, were employed to image dynamic cell culture experiments *in-situ* in a bioreactor. Other advances in computational modeling of single cell forces and cell populations were carried out to predict normal ossification patterns and cartilage formation. By combining information from different techniques on the same sample and visualizing structure using interactive, immersive visualization techniques, scientists will gain new insights into the physics and materials science of complex systems.

Nanobiosensing

Research in this focus area concentrates on the development of techniques to measure and manipulate biological atoms, molecules, and macromolecules at the nanoscale level (1–100 nm). Mechanical tools including an optical trap and bioMEMS devices that can be integrated with currently used biological techniques for evaluating and measuring cellular response (i.e., gene expression, cell morphology, area of adhesion) were developed. Additional studies focus on identifying mechanical forces that indicate the onset of osteogenesis and angiogenesis.

Contact: Eric J. Amis

Combinatorial Methods for Rapid Characterization of Cell-Surface Interactions

The increasingly complex nature of functional biomaterials demands a multidisciplinary approach to identify and develop strategies to both characterize and control cell-material interactions. A robust framework outlining the interactions governing biomaterial performance does not exist but is desperately needed. This project provides the basis for this framework by focusing on fabrication of single and multi-variable continuous combinatorial libraries to rapidly identify compositions and physical properties exhibiting favorable cell-material interactions.

Matthew L. Becker and Lori A. Henderson

Developmental biology and tissue engineering are avenues of research that must be fully integrated to realize the opportunities in regenerative medicine. For example, while the interactions between cell and extracellular matrix have been studied extensively, much less is understood regarding the influence of synthetic materials. There is little doubt that having good control of surface morphology as well as advanced high-throughput (HT) metrologies for analyzing cell-surface interactions are needed for biological interpretations, and while chemical and topographical manipulations of surfaces have been established, HT methods to evaluate biological responses to these manipulations have not. For these reasons, we are developing metrologies and HT platforms to rapidly analyze physicochemical, mechanical, and material properties of biomaterials. We provide examples of two of our sample fabrication methods, distinct from traditional self-assembled monolayer approaches, that are being used to design, manipulate, and quantify cell-surface interactions.



Figure 1: AFM micrographs of the tyrosine-derived polycarbonate homopolymers and discrete blends show compositionally dependent phase separation, which is reflected in the immuno-fluorescent staining for actin (red, cell spreading) and vinculin (green, focal adhesion contacts) on MC3T3-E1 osteoblasts.

Two functional polymer surfaces, phase separated tyrosine-derived polycarbonate blends (DTR-PC) and conformational-based poly(2-hydroxyethyl methacrylate) brushes [poly(HEMA)], were analyzed using combinatorial methodologies. The DTR-PC films, consisting of homopolymer and discrete composition blends of tyrosine-derived polycarbonates, were shown to have compositionally dependent gene expression profiles with the blends differing significantly from the respective homopolymers. Figure 1 illustrates the effect that polymer blending has on cell spreading; the extension and distortion of the lamellapodia increase and the cells appear to spread less in the blend samples with increasing DTO content. The surface properties from these discrete films will be used to establish correlations and limitations for comparing measurements from discrete samples and single and multi-variable continuous gradient substrates.

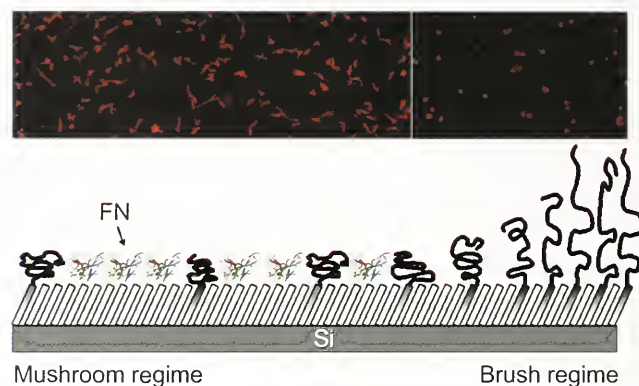


Figure 2: Schematic representation of the poly(HEMA)-FN gradient and Fibroblast cell distribution.

Poly(HEMA) gradients were prepared to study molecular interactions and cell conformation on fibronectin (FN) coated poly(HEMA) by combining “controlled” free radical polymerization with gradient preparation technology. This gradient covers “mushroom” to “brush” regimes in order to determine how grafting density influences protein adsorption and cellular response as shown in Figure 2. The number of cells, their shape, and size were thus correlated to the density of fibronectin across the gradient.

In summary, the tools developed in this program will enable the design of material libraries to be used to probe the behaviors of cells.

Contributors and Collaborators

N.D. Gallant, L.O. Bailey, C. Simon, Jr., T.W. Kee, Y. Mei, J.S. Stephens, E.J. Amis (Polymers Division, NIST); K. Langenbach, J.T. Elliot (Biotechnology Division, NIST); J. Kohn, A. Rege, J. Schutt (Rutgers University & The New Jersey Center for Biomaterials)

Cell Response to Tissue Scaffold Morphology

Industrial and regulatory sectors have expressed a need for standards and new metrologies relating to properties of tissue scaffolds for regenerative medicine. We seek to meet these needs in several areas where the criteria are clear, and to help clarify industrial and regulatory needs in other areas where such clarification is required. We are developing a reference scaffold for porosity and permeability. Also, we are developing metrologies for establishing the relationship between scaffold porosity/morphology and cell response, for assessing the ability of a tissue scaffold to safely host cytokine, and for quantifying mechanical stimulation requirements for cells — at the cellular level — from macroscopic inputs.

Marcus T. Cicerone

In the field of regenerative medicine, one seeks to guide cell differentiation and proliferation, and production of the extracellular matrix through functional properties of 3D tissue scaffolds. Developing the ability to guide such cell behaviors requires first the ability to characterize and assess properties of tissue scaffolds as they relate to cell response. This, in turn, requires well-defined physical and biological systems for which quantitative rules can be formulated and verified.

We are developing methods for quantitatively characterizing tissue scaffolds and the cellular responses they elicit. There are three classes of scaffold properties that we focus on relative to their impact on cell behavior; these are: (i) morphological/topological properties, (ii) mechanical properties, and (iii) ability of biodegradable scaffold materials to act as biopreservants in connection with hosting growth factors and other cytokines.

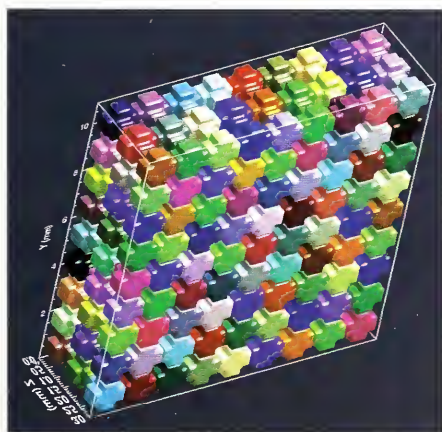


Figure 1: A reconstruction of a candidate reference scaffold, generated from a tomographic image. Each colored object represents a separate unit cell within the pore structure of the scaffold.

We led a worldwide collaboration under ASTM with 17 other laboratories to establish a series of reference scaffolds for porosity and permeability. Our primary characterization method for these scaffolds is based on tomographic image analysis of scaffold morphology.

We are developing metrologies for assessing osteoblast response to pore size distributions in tissue scaffolds based on extracellular matrix (ECM) production. We are also investigating morphology effects on osteoblast response to surface chemistry. The image analysis methods developed in the reference scaffold activity serve to support these efforts. The ability to uniformly and reproducibly seed 3D scaffolds with adherent cells is another critical factor for quantifying links between scaffold morphology and cell response, and we have developed methods to accomplish this.

We are using computational modeling coupled with high-resolution imaging, atomic force microscopy (AFM), and optical trapping to develop metrology in the area of cell response to environmental mechanical stresses. It is clear that mechanical stimulation is required for some cell types to differentiate properly. Thus, it is important to be able to measure precisely what stress conditions are necessary for proper phenotypic expression for selected cell types. We are collaborating with the Materials Reliability Division of MSEL to establish methods to quantify the stress conditions at the cellular level based on macroscopic forces placed on the scaffold construct. Our approach is to translate ranges of macroscopic stresses to local stresses experienced by cells using a finite element model. These local stresses will be correlated with cell response in terms of ECM production.

Biopreservation of cytokines in tissue scaffolds is a complex but important area of regenerative medicine that has been historically underserved. We are collaborating with six academic and one national lab to create a holistic approach to stabilizing proteins in solid hosts such as tissue scaffolds. We are leading the grant-writing efforts in this collaboration and are focusing on clarifying the relationship between fast glassy dynamics and biopreserving ability of a material, which we have already observed in neutron scattering experiments. In keeping with this goal, we are establishing accessible time-resolved optical metrologies for measuring these dynamics.

Contributors and Collaborators

J. Dunkers, F. Wang, J. Cooper, T. DuttaRoy, J. Stephens, F. Phelan, M.Y.M. Chiang, L. Henderson (Polymers Division, NIST); Tim Quinn (Materials Reliability Division, NIST)

3-Dimensional *In Situ* Imaging for Tissue Engineering: Exploring Cell/Scaffold Interaction in Real Time

Real time investigations of cell/scaffold interactions provide valuable information about the dynamic nature of cells and their spatial arrangements with respect to the three-dimensional (3D) architecture of tissue engineering scaffolds. In situ imaging capabilities will enable determination of the structure/function relationship of tissue engineering scaffolds and definition of the necessary properties to promote tissue regeneration. We demonstrate tools for in situ imaging of cells/scaffold interactions.

Jean S. Stephens and Joy P. Dunkers

The ability to image live cells and their corresponding interactions with the surrounding environment provides critical information about the ability to promote desired cellular activity (proliferation, differentiation, etc.) for tissue regeneration. In order to develop *in situ* optical imaging capabilities, we must be able to nondestructively and noninvasively image the interactions at the cell/scaffold interface while maintaining cell viability.

In our laboratory, collinear optical coherent microscopy/confocal fluorescence microscopy (OCM/CFM) has successfully been used to image the 3D interconnected porous structure of polymeric scaffolds. This system combines high spatial resolution ($\sim 1 \mu\text{m}$), high sensitivity ($>100 \text{ dB}$), and exceptional depth-of-penetration associated with OCM with the

fluorescent capabilities of CFM. This, therefore, allows us to not only investigate the 3D scaffold, but also the use of conventional fluorescent staining techniques to evaluate cellular response.

In order to perform live cell imaging, a system or bioreactor that can sustain cell viability outside of an incubator and allow for imaging was constructed (Figure 1). The bioreactor is a perfusion flow bioreactor. This design forces the media to flow through the scaffold, therefore ensuring nutrient delivery and oxygen perfusion, as well as waste removal, throughout the entire structure. Also, a dynamic cell culture creates an environment that better mimics physiological conditions. The temperature of the bioreactor system is maintained by circulating water (37°C) through a copper element.

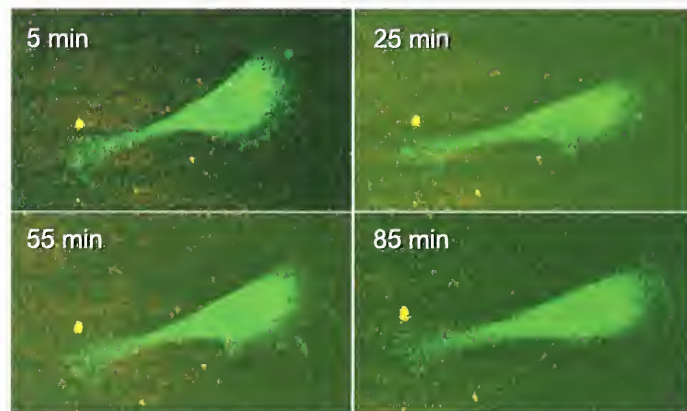


Figure 2: Time-lapse images of cell movement.

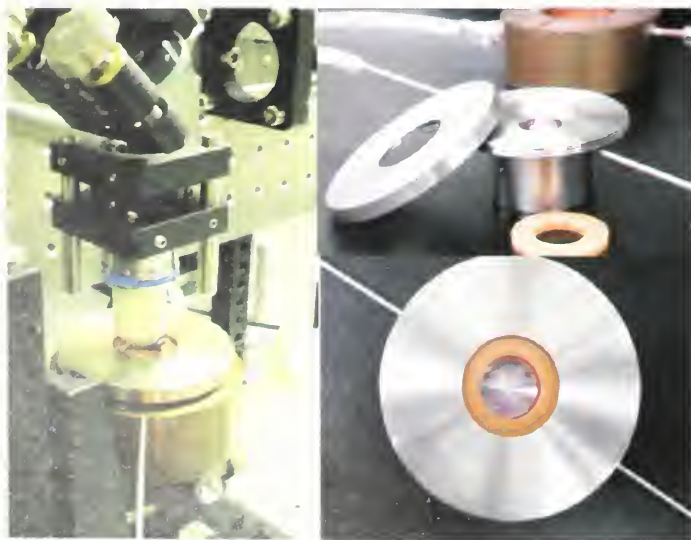


Figure 1: Bioreactor in OCM/CFM, open and top view.

Initial *in situ* imaging studies indicate the maintenance of cell viability, and we have successfully imaged cells for several hours. The series of images in Figure 2 illustrate cell movement over a 2 hour time period. The ability to collect images in real time will give a great insight and understanding of how cells are responding to different materials, scaffold architectures, and culture conditions. These data will provide new metrics for the evaluation of tissue engineering scaffolds.

Contributors and Collaborators

J.A. Cooper, C.R. Snyder (Polymers Division, NIST)

Broadband CARS Microscopy for Cellular/Tissue Imaging

In many of the biological sciences, as well as in many areas of polymer science, there is a need for high-resolution, noninvasive, and chemically sensitive imaging. We have developed a broadband coherent anti-Stokes Raman scattering (CARS) microscopy that provides an unprecedented combination of imaging speed and spectral coverage (i.e., chemical sensitivity). Our current efforts are focused on eliminating nonresonant background effects, which can limit sensitivity of the technique.

Marcus T. Cicerone

We have developed a broadband CARS microscopy method which allows us to obtain vibrational spectra in the range (500 to 3000) cm^{-1} in less than 1/50th the time required to obtain similar spectra by spontaneous Raman. This development was reported at the first meeting of National Institute for Biomedical Imaging and Bioengineering (NIBIB) grantees, in Bethesda, Maryland, the 11th Annual Time Resolved Vibrational Spectroscopy Conference, and the 2005 Biophysical Meeting.

One key to the method we have developed is the generation of a broadband continuum. Optical pumping of a tapered silica fiber was used to generate broadband continuum in the first prototype of this instrument. Accumulative photo-damage limits the lifetime of the tapered fiber, and seriously limits the power level of the light that can be generated, significantly restricting the taper fiber as a reliable light source for CARS microscopy. With the assistance of an outside vendor, we have designed and procured a photonic crystal fiber (PCF) that is sealed at the ends, and which avoids the above issues. The PCF did not show any sign of degradation after a month, under long-term irradiation of 40 kW peak power femtosecond laser pulses. This advance provided ≈ 10 -fold increase in signal levels, so that, in principle, we can gather broadband spectra in 1/500th the time required for spontaneous Raman spectroscopy. In practice, this rate exceeds the capabilities of the CCD camera, which therefore sets the limits on data acquisition; a faster camera would allow higher data collection rates.

A blend of chemically similar biodegradable polymers, abbreviated as DTE and DTO (see Figure 1a), have induced remarkable low immune response upon fibroblast cell adhesion. These two polymers phase-separate upon annealing, and since they have similar indices of refraction, optical microscopy cannot be used to image the phase-separated domains. On the other hand, broadband CARS microscopy has the sensitivity to distinguish the two polymers. Figure 1 shows the three-dimensional imaging of a 50/50

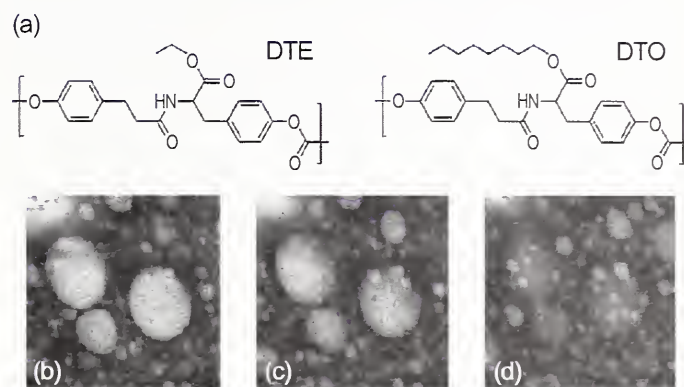


Figure 1: (a) Chemical structures of DTE and DTO. CARS images of a 50/50 DTE/DTO blend at depth: (b) 0 μm , (c) 3 μm , (d) 6 μm . The white areas in these images are DTO; the black regions are DTE.

DTE/DTO blend sample. In this sample, the spatial resolution is approximately 0.4 μm . We are currently exploring the hypothesis that the low cellular immune response to the blends has its origins in spatial patterning of the adhesion proteins. We are working to correlate the protein adsorption with spatial patterning of DTO and DTE rich domains.

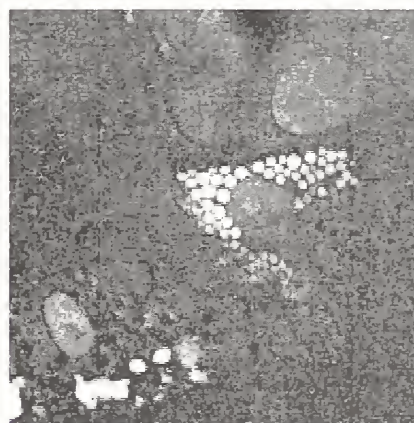


Figure 2: Micrograph of adipocyte. This image was obtained without the use of contrast agents such as fluorescent stains; the 2845 cm^{-1} C-H stretch vibrational band was the only image contrast.

In Figure 2, bright circular features are triglyceride lipid droplets in adipocytes, and the more subdued quasi-circular objects are the cells. We were unable to image the presence of protein in the cytosol due to nonresonant background. Detection of these proteins is crucial to identifying cell type, and we are currently focusing our efforts on substantially reducing the effects of nonresonant background.

Contributors and Collaborators

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Molecular Design and Combinatorial Characterization of Polymeric Dental Materials

Polymeric dental materials are finding increasing applications in dentistry and allied biomedical fields. As part of a joint research effort supported by the National Institute of Dental and Craniofacial Research and also in collaboration with the American Dental Association Health Foundation Paffenbarger Research Center, NIST is providing the dental industry with a fundamental knowledge base that will aid in the prediction of clinical performance of dental materials.

Joseph M. Antonucci and Sheng Lin-Gibson

In contrast to current methods that rely on lone-specimen-at-a-time measurements, metrologies based on combinatorial and high-throughput (C&HT) approaches can accelerate fundamental and applied research in dental materials. For dental polymers and their derivatives (sealants, adhesives, restorative composites), many critical properties depend on the chemical, structural, and compositional nature of the initial monomer (resin) system. For multiphase dental materials, *e.g.*, composites, similar factors govern the quality of the interphase between the silanized filler phase and the resin matrix. The objective of this research was to determine the feasibility of adapting C&HT techniques to measure material properties and screen various experimental resin chemistries for molecular design of novel dental polymers and composites. The technologies developed to enable this research include nanoindentation and the fabrication of single component or multi-variable discrete and continuous gradient films.

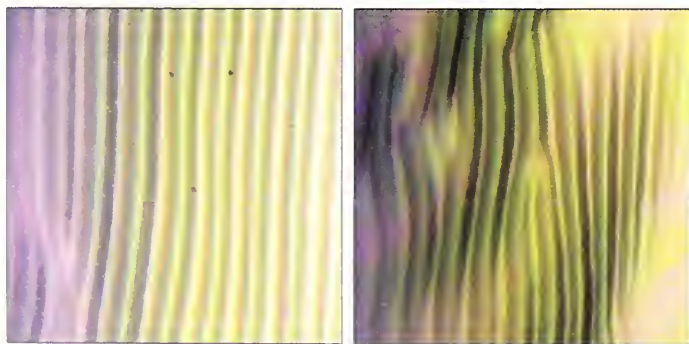


Figure 1: Buckling patterns of BisGMA-TEGDMA in mass ratios of 30:70 (left) and 70:30 (right).

Among the different resin chemistries under investigation, 2D compositional gradients using BisGMA-TEGDMA were selected as the benchmark for developing metrologies and rapid screening techniques for optimizing hardness, shrinkage, and biocompatibility. The elastic modulus was determined by two methods, nanoindentation and SIEBIMM — a strain-induced elastic buckling

instability for mechanical measurements test. SIEBIMM on PMMA, a linear polymer, yielded a modulus comparable to that obtained by the 3-point bend test. Buckling patterns from cross-linked BisGMA/TEGDMA films (Figure 1) resulted in moduli with increased variability, *i.e.*, the buckling patterns were not straight, parallel lines. Reasons for this behavior are under study.

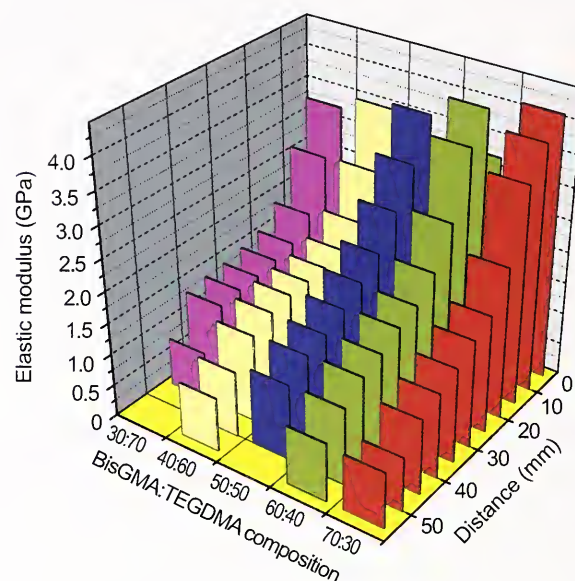


Figure 2: Elastic moduli of photopolymerized BisGMA-TEGDMA of different compositions as a function of irradiation time (represented as distance).

BisGMA-TEGDMA networks with 2D gradients, varying in monomer composition and conversion, were fabricated with a broad conversion range for all monomer compositions. Conversions were measured using near-IR spectroscopy, and elastic modulus and hardness. As shown in Figure 2, the conversion and the mechanical properties correlated well.

Additional techniques with the potential for C&HT approaches are being evaluated for their ability to screen other properties of dental materials, including the interfacial silane chemistry and cellular response. Studies on the interfacial chemistry have shown that covalent bonding of nanoparticles with the polymerized matrix resulted in well-dispersed composites. To screen the biological response to dental materials, methods to measure cell viability, apoptosis, and gene expression levels as a function of vinyl conversion have been developed.

Contributors and Collaborators

E.A. Wilder, K.S. Wilson, N.J. Lin, C.M. Stafford, L. Henderson (Polymers Division, NIST); P.L. Votruba-Drzal (Materials and Construction Research Division, NIST)

Safety and Reliability

We take for granted that the physical infrastructure around us will perform day in and day out with consistent reliability. Yet, failures occur when these structures degrade to where they no longer sustain their design loads, or when they experience loads outside their original design considerations. In addition, we have become increasingly aware of our vulnerability to intentional attacks. The Safety and Reliability Program within MSEL was created to develop measurement technology to clarify the behavior of materials under extreme and unexpected loadings, to assess integrity and remaining life, and to disseminate guidance and tools to assess and reduce future vulnerabilities.

Project selection is guided by identification and assessment of the particular vulnerabilities within our materials-based infrastructure, and focusing on those issues that would benefit strongly by improved measurements, standards, and materials data. This year, we have worked with the Department of Homeland Security and the Office of Science and Technology Policy in developing the National Critical Infrastructure R&D Plan, which will provide guidance across much of the national infrastructure. Ultimately, our goal is to moderate the effects of acts of terrorism, natural disasters, or other emergencies, all through improved use of materials.

Our vision is to be the key resource within the Federal Government for materials metrology development as realized through the following objectives:

- Develop advanced measurement methods needed by industry to address reliability problems that arise with the development of new materials;
- Develop and deliver standard measurements and data;
- Identify and address vulnerabilities and needed improvements in U.S. infrastructure; and
- Support other agency needs for materials expertise.

This program responds both to customer requests (primarily other government agencies) and to the Department of Commerce 2005 Strategic Goal of “providing the information and framework to enable the economy to operate efficiently and equitably.” For example, engineering design can produce safe and reliable structures only when the property data for the materials are available and accurate. Equally important, manufacturers and their suppliers need to agree on how material properties should be measured.

The Safety and Reliability Program works toward solutions to measurement problems on scales ranging

from the macro to the micro. The scope of activities includes the development and innovative use of state-of-the-art measurement systems; leadership in the development of standardized test procedures and traceability protocols; development of an understanding of materials in novel conditions; and development and certification of Standard Reference Materials® (SRMs). Many of the tests involve extreme conditions, such as high rates of loading, high temperatures, or unusual environments (*e.g.*, deep underwater). These extreme conditions often produce physical and mechanical properties that differ significantly from handbook values for their bulk properties under traditional conditions. These objectives will be realized through innovative materials property measurement and modeling.



The MSEL Safety and Reliability Program is also contributing to the development of test method standards through committee leadership roles in standards development organizations such as the ASTM International and the International Standards Organization (ISO). In many cases, industry also depends on measurements that can be traced to NIST SRMs.

In addition to the activities above, MSEL provides assistance to various government agencies on homeland security and infrastructural issues. Projects include assessing the performance of structural steels as part of the NIST World Trade Center Investigation, collaborating with both the Department of Transportation and the Department of Energy on pipeline safety and bridge integrity issues, advising the Bureau of Reclamation on metallurgical issues involving pipelines and dams, and advising the Department of the Interior on the structural integrity of the *U.S.S. Arizona* Memorial.

Contact: Chad R. Snyder

Polymer Reliability and Threat Mitigation

This project is developing metrologies and predictive models to test and predict the long-term reliability of polymers used in ballistic resistant armor and machine readable travel documents. Use of these methods and models will enable one to monitor the performance of polymeric materials while in use, elucidate how environmental and mechanical factors influence performance, and provide a basis for estimating durability and establishing care procedures.

**Chad R. Snyder, Gale A. Holmes, and
Walter G. McDonough**

Ballistic Resistant Armor

In response to an apparent failure of ballistic resistant armor during first responder use, NIST's Office of Law Enforcement Standards initiated a research program designed to strengthen the certification process of these protective devices. We are working to identify and develop analytical metrologies for quantifying the mechanical properties and degradation pathways of ballistic fibers that comprise this armor, with the ultimate goal being an estimate of vest durability and care procedures.

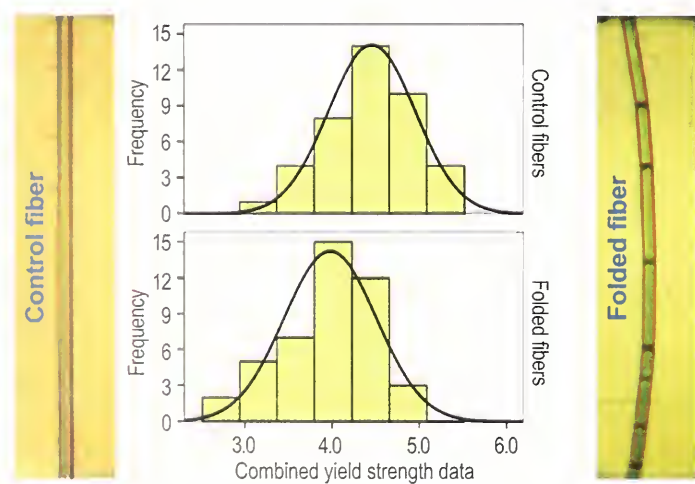


Figure 1: Top and Left: Micrograph and yield strength data obtained from modified single fiber test on an unfolded PBO fiber; Bottom and Right: Micrograph and figure for a folded PBO fiber.

This year, we have made considerable progress on multiple fronts towards these goals for poly(benzoxazole) (PBO) ballistic fibers. The modified single fiber fragmentation test, developed last year, was used to examine the effect of fiber fatigue on ballistic resistance. Figure 1 shows the effect of folding on the morphology and mechanical properties of a PBO fiber. Our analysis suggests that, for this case, folding resulted in an estimated >10 % reduction in overall ballistic performance,

as quantified through the method of Cuniff and Auerbach.^[1] Ongoing research is examining the effects of fold radius as well as the effects of repeated folding.

Complementing our mechanical properties studies, our research into the degradation pathways of PBO and PBO-like materials has made significant headway. In addition to completion of our review article,^[2] we have synthesized the model compounds 2-phenylbenzoxazole and bis-1,4-(2-benzoxazolyl) phenylene, and their hydroxy analogs, and we are currently analyzing, through matrix assisted laser desorption/ionization (MALDI) mass spectrometry, the degradation products resulting from exposure to our newly acquired solar simulator.

Machine Readable Travel Documents

As indicated in an October 14, 2004 press release from the U.S. Government Printing Office (GPO), NIST is testing the candidates for the new U.S. electronic passports for their ability to meet durability, security, and electronic requirements. This new technology will eventually be incorporated into electronic U.S. passports to enhance the security of millions of Americans traveling around the world. At the request of the U.S. Department of State, we participated in the WG3 (Working Group 3 of ISO) meeting of the *Document Durability Task Force for the EPassport* in Tsukuba, Japan. The purpose of the task force meeting was to update the participants on the status of the Test Specification for Machine Readable Travel Documents (MRTD). The main recommendation from the meeting was that any proposed test specification by ISO would serve as the guideline to help nations writing requests for proposals to develop their own MRTDs. Also, the task force chairs have decided to use more complex testing sequences to better represent real-world applications; this was in line with the recommendations made by NIST.

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 Craniofacial tissue engineering
 Cell migration

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Crystallization and melting of miscible
 polymer blends
 Ionomers
 Optical coherence microscopy
 Tissue engineered scaffolds
 Static small angle laser light scattering

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X-ray reflectivity
Small-angle neutron scattering
Nanoimprint lithography
Structural characterization of low dielectric
constant thin films
Porosimetry of porous thin films

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Dielectric relaxation spectroscopy
Nanocomposites
Atomic force microscopy
Rubber-toughened phenolic resins
Dynamic mechanical analysis of polymer blends

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Polymer thin films and interfaces
Polymer photoresists for lithography
Organic electronics
Nanoimprint lithography
Small angle x-ray and neutron scattering
Statistical mechanics
X-ray and neutron reflectivity

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Combinatorial screening of scaffolds
Cellular response to materials

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Rheology of gels and nanocomposites
Mass spectrometry of synthetic polymers
Polymer synthesis and modification
Structure and dynamics of nanocomposite
polymeric materials
Tissue engineering hydrogels

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Polymer synthesis
Thermal gravimetric analysis
Differential scanning calorimetry
Gel permeation chromatography
Infrared spectroscopy
Nuclear magnetic resonance

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Calcium phosphate chemistry
Biomineralization (normal and pathological)
Crystal growth and dissolution kinetics
Heterogeneous equilibria

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Processing and cure monitoring polymer
composites
Failure and fracture of polymers
Polymer composite interfaces
Dental materials

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Atomic force microscopy
Viscoelastic properties
Surface force measurements

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Polymer synthesis
Peptide synthesis
Biodegradable polymers
Biomimetic polymers

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Polymer rheology
Characterization of processing aids

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Effects of shear and pressure on phase behavior
Fluorescence and optical monitoring of
polymer processing
Liquid crystals
Shear-induced two phase structures
Polymer slippage

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Polymer Formulations
Water soluble polymers
Microemulsions
Neutron and x-ray scattering from polymers

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Dielectric relaxation spectroscopy
Electronic properties of polymers and
composites
Electronic packaging
Microwave and optical waveguides
Photoelectron spectroscopy (x-ray and UV)
Reliability, stress testing

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Dental appliance and crown and bridges
fabrication
Machine shop applications

Pathak, Jai A.⁺**jai.pathak@nist.gov**Rheology and linear viscoelasticity
Polymer dynamics and complex fluids
Microfluidics**Phelan, Jr., Frederick R.****frederick.phelan@nist.gov**Composites processing
Microfluidics
Viscoelastic flow modeling
Chaotic mixing
Flow in porous media
Lattice Boltzmann methods**Prabhu, Vivek M.****vivek.prabhu@nist.gov**Small-angle neutron scattering
Polyelectrolytes
Polymers for lithography
Fluorescence correlation spectroscopy
Polymer thin films
X-ray and neutron reflectivity**Quinn, Janet*****janet.quinn@nist.gov**Fractography
Dental materials and material properties
Composites**Richards, Nicola*****nicola.richards@nist.gov**Dental restorative materials
Polymer matrix composites**Rao, Ashwin B.⁺****ashwin@nist.gov**Polymer adsorption
Thin films gels
Fluorescence microscopy
Interfacial rheology**Ro, Hyun Wook⁺****hyun.ro@nist.gov**Nanoimprint lithography
Low-k dielectric thin films
X-ray reflectivity**Sambasivan, Sharadha⁺****sharadha@bnl.gov**Near-edge x-ray absorption fine structure spectroscopy (NEXAFS)
Polymers for lithography
Polymer relaxation and tribology
Self assembled monolayer orientation
Catalyst surface and bulk characterization**Schumacher, Gary E.*****gary.schumacher@nist.gov**Clinical dentistry
Composites
Dentin adhesives**Simon, Carl G., Jr.****carl.simon@nist.gov**Biocompatibility
Cytotoxicity
Signaling in human platelets
Bone marrow cell lineage/trafficking
Combinatorial methods**Skrtic, Drago*****drago.skrtic@nist.gov**

Bioactive amorphous calcium phosphate-based dental materials

Smith, Jack R.**jack.smith@nist.gov**Surface science
Computational modeling
Biomaterials characterization**Snyder, Chad R.****chad.snyder@nist.gov**Polymer crystallization
WAXD and SAXS of polymeric materials
Thermal expansion measurements
Thermal analysis
Thermal management
Dielectric measurements and behavior
Ballistic resistance**Soles, Christopher L.****csoles@nist.gov**Polymer dynamics
Inelastic neutron scattering
Low-k dielectric thin films
X-ray and neutron reflectivity
Polymer thin films and lithography
Ion beam scattering
Nanoimprint lithography**Stafford, Christopher M.****chris.stafford@nist.gov**Combinatorial and high-throughput methods
Polymer thin films
Polymer adhesion
Mechanical properties of thin films
Surfaces and interfaces**Start, Paul R.⁺****paul.start@nist.gov**Nanocomposites
Transmission electron microscopy
Sol-gel processes
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Fiber-matrix interfacial shear strength
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Cell and tissue mechanics
Mechanoactive bioreactors
Tissue engineering

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Crystallography
X-ray diffraction
Calcium phosphate biomaterials
Topical fluoridation
De- and remineralization

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Characterization: biomaterials; physical and mechanical properties
Reference biomaterials
Reference data for biomaterials
Biomaterials: orthopaedics, cardiovascular, dental, ophthalmic, & tissue engineered medical devices
Standards for medical devices

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Chemistry of calcium phosphate and peroxide compounds
Remineralization studies
Standard reference materials

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Measurement of orientation in polymer fibers and films
Solid-state NMR of polymers
Measurement of polymer morphology at the 2–50 nm scale
Pulsed field gradient NMR

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Polymer synthesis
Combinatorial methods
Drug delivery
Organic electronics
Polymer thin films
Self-assembled monolayers

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Dental plaque chemistry
Chemistry of calcium phosphates
Microanalytical techniques
Fluoride chemistry

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Polymer thin film properties
X-ray and neutron reflectivity
Polymers for lithography
Quartz crystal microbalance
Ordered mesoporous materials
Organic electronics

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Mass spectrometry
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Photophysics and photochemistry of polymers
Fluorescence spectroscopy
Cure monitoring of polymerization
Tissue engineering

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Monte Carlo simulations
Finite element modeling
Polymer composites
Mechanical properties
Image quantitation

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Biomaterials
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Growth factor dynamics and cellular response in biomaterials

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Mass spectrometry of polymers
Chemometrics
Size exclusion chromatography

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Rheological behavior of polymer gels

Mechanical properties of polymer composites

Structure-property relationships

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Neutron and x-ray scattering and reflectivity

Electron microscopy

Mechanical behavior of polymers and
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Polymer surfaces and interfaces

Polymer networks

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Polymer formulations

Polymer synthesis

Interfacial tension measurements

Combinatorial and high-throughput methods

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Combinatorial and high-throughput methods

Polymer formulations

Surface polymerization

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Bone tissue engineering

Scaffold and cell interactions

Fiber and whisker composites

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Combinatorial and high-throughput informatics

Database structure

Laboratory automation

Polymer thin films and blends

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Computed fluid dynamics

Data acquisition

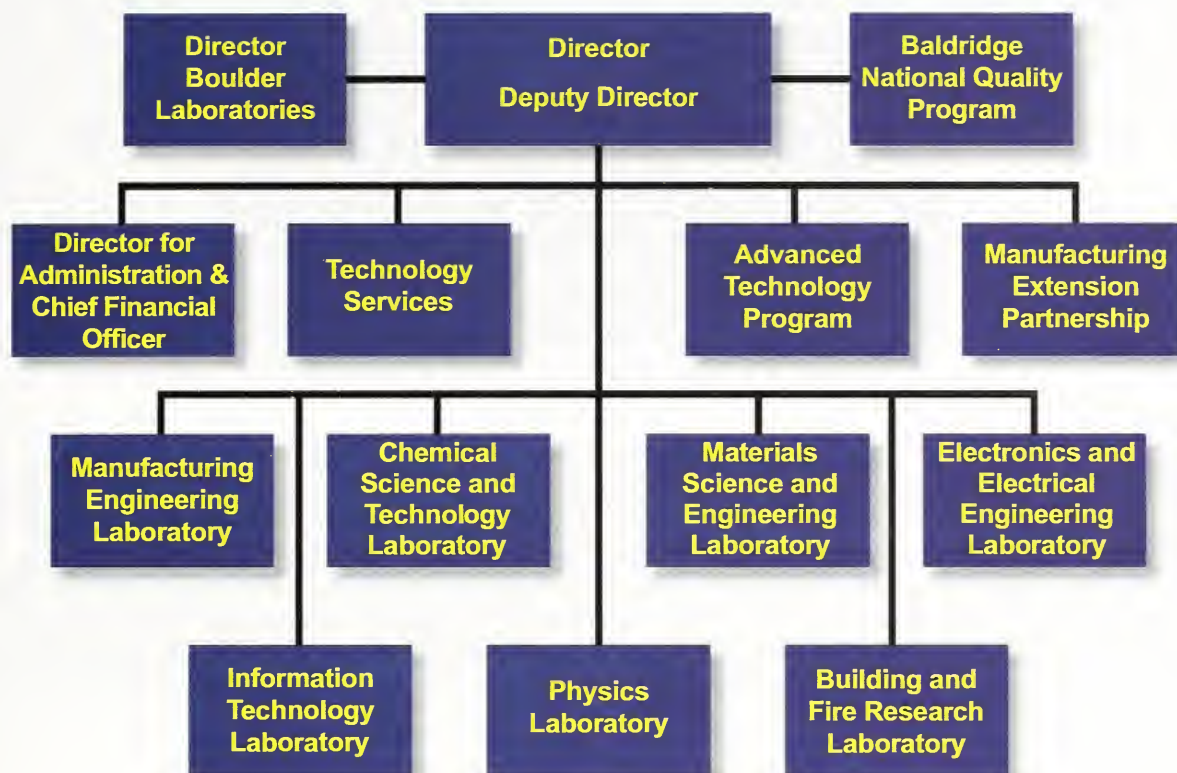
Multivariate analysis

Signal processing

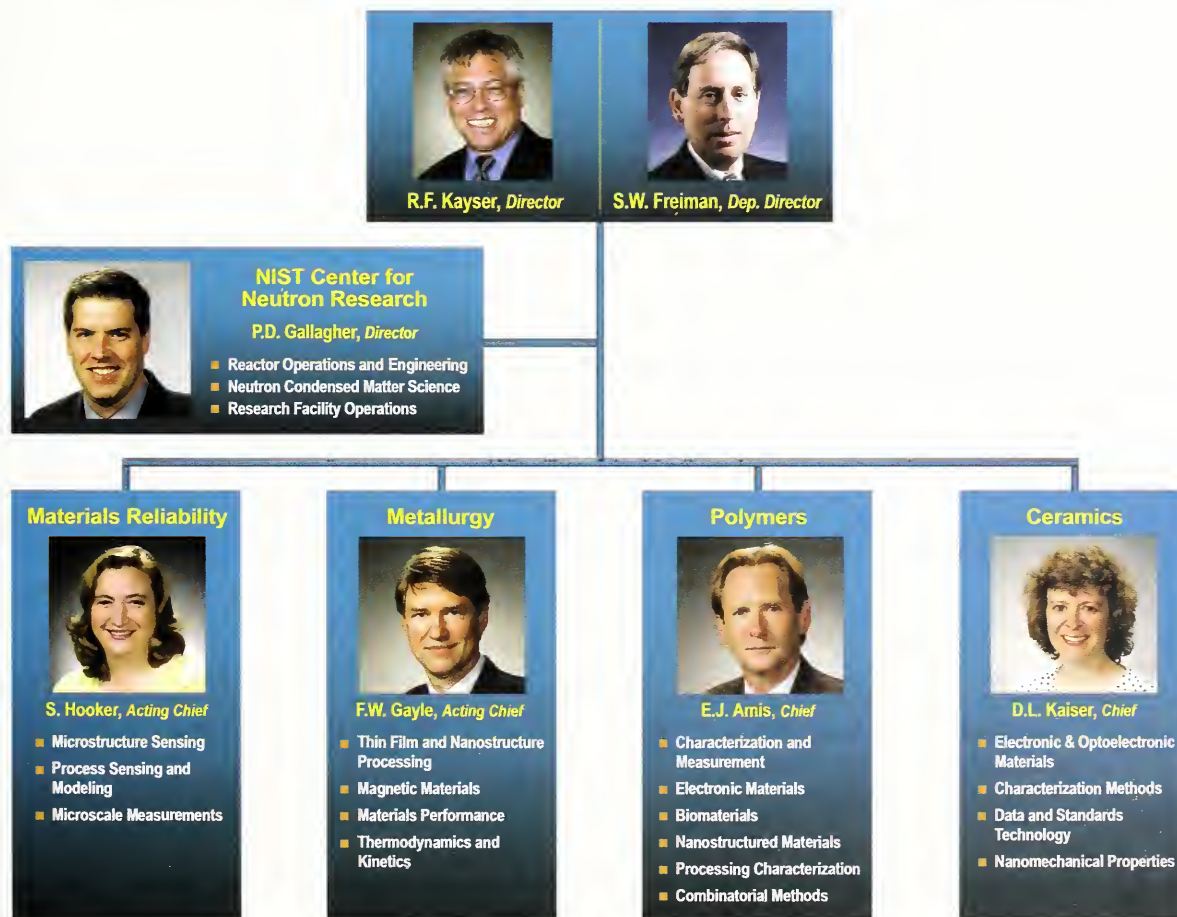
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Multiphase Materials (854.04)

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